JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

1910. Vol. XCVIII. Part I.

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1910.

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ERRATA.

Vol. XCVI (Abstr., 1909).

Page	Line	Col.	
1185	15–16*	ii	*insert* "**Tilden** (*Sir*) *William Augustus*, Mendeléeff memorial lecture, T., 2077."

Vol. XCVIII (Abstr., 1910).

Part I.

Page	Line		
i, 14	12	*for*	"*Decalene* ακ-*dithiol*" read "*Decylene* ακ-*dithiol*."
i, 58	1		
i, 58	3	,,	"4-chloroxanthone" *read* "3-chloroxanthone."
i, 58	9		
i, 58	16	,,	"4-*bromoxanthone*" read "3-*bromoxanthone*."
i, 89	9	,,	"$C_8H_{13}O_2Br$" *read* "$C_7H_{12}O_2$."
i, 141	10	,,	"$C_{12}H_5ON_4Cl_4$" *read* "$C_{12}H_5ON_3Cl_4$."
i, 141	14		
i, 141	19, 20	,,	"-2:1:3-*benztetrazole*" read "-2:1:3-*benztriazole*."
i, 214	5*		
	2*	,,	"*dl*-Hydroxyerythronic acid" *read* "*dl*-oxyerythronic acid.'
i, 215	3		
	6		
i, 260	18*	,,	"*Sulphonyldibenzoic*" read "*Sulphinyldibenzoic*."
i, 311	1*	,,	"Abstr., 1909, i, 4" *read* "this vol., i, 4."
i, 330	2	,,	"Henrichsen" *read* "Hinrichsen."
i, 350	9*	,,	"Jose R. Carracido" *read* "Jose Rodriguez Carracido."
i, 351	8	,,	"932" *read* "934."
i, 357	6	,,	"*ethyl anilino-*" read "*ethylanilino-*."
i, 371	14*	,,	"2:4-*Dinitrophenyl*-dl-*leucine*" read "*Chloro*-2:4-*dinitro*-dl-*leucine*."
i, 376	11*	,,	"$C_6H_4\langle{}^{CH}_{C(OH)}\rangle C_6H_2(OH)_2{\cdot}SO_3Na$" *read* "$C_6H_4\langle{}^{CH}_{C(OH)}\rangle C_6H(OH)_2{\cdot}SO_3Na$."
i, 415	19	,,	"Julius" *read* "Johannes."
i, 433	17	,,	"ω-*Bromo*-" read "ω-*Chloro*-."
i, 435	1	,,	"1-*phenyl*-3-*methyl*-5-*hydroxymethylpyrazolone*" read "1-*phenyl*-3-*methyl*-5-*hydroxymethylpyrazole*."
i, 471	21	,,	"*acetyl*-p-*nitrophenylethylmethylamine*" read "*acetylphenylethyl-*

Vol. 98 (Abstr., 1910).

i. 532	6*	,,	"When X" *read* "When R."
	3*	,,	"magnesium derivative of bromoquinol dimethyl ether" *read* "bromomagnesium derivative of quinol dimethyl ether."

$\overset{|}{C}Me_2{\cdot}OH$ $\overset{|}{C}Me_2{\cdot}OH$.

i, 574	10*		
	9*	*delete*	commas preceding and following "however."
i, 882	21*		
	25*	*for*	"9:10-Dimethylphenanthridene" *read* "9:10-Dimethylphenanthridine."

* From bottom.

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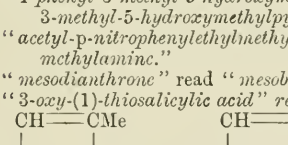
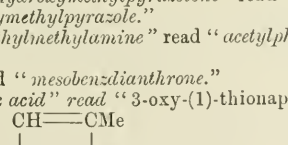
i, 471	21	,,	"*acetyl*-p-*nitrophenylethylmethylamine*" read "*acetylphenylethylmethylamine*."
i, 495	6	,,	"*mesodianthrone*" read "*mesobenzdianthrone*."
i, 500	16*	,,	"3-*oxy*-(1)-*thiosalicylic acid*" *read* "3-oxy-(1)-thionaphthen."
i, 574	16*	,,	 *read* 
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	25*		

* From bottom.

PART II.

Page	Line	
ii, 81	22	*for* "SUZUKII" *read* "SUZUKI."
ii, 120	2*	,, "28 atmospheres" *read* "280 atmospheres."
ii, 162	14	,, "1910" *read* "1909."
ii, 250	20	,, "23—32" *read* "23—37."
ii, 366	2*	,, "much less" *read* "much more."
ii, 381	11	,, "BAUER" *read* "BAUR."
ii, 410	3	,, "1910" *read* "1909."
ii, 501	17*	,, "CASTELLANA" *read* "CASTELLANI."
ii, 572	25	,, "in water vapour" *read* "as water vapour."
ii, 578	25	,, "effect" *read* "affect."
ii, 581	9	,, "$\beta\gamma$" *read* "$\beta\nu$."
ii, 581	18	,, "$A = -T\int Q/T_2 dT$" read "$A = -T\int QT_2 dT$."
ii, 630	18	,, "potassium" *read* "calcium."
ii, 668	16	,, "Grignard" *read* "Guignard."
ii, 707	18	,, "ii, 557" *read* "ii, 120."
ii, 747	17	,, "ALEXANDRON" *read* "ALEXANDROFF."
ii, 793	4*	,, "Newton" *read* "Overton."
ii, 796	19*	,, "alcaptan" *read* "alcapton."
ii, 799	20 / 24	,, "*plymonthiensis*" read "*plymouthiensis.*"
ii, 838	4*	*insert* "sodium" *before* "dihydrogen."
ii, 1129	23*	(column 1) *for* "**Arnold**, *W.*," *read* "**Arnold**, *Vinzenz.*"

* From bottom.

JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Electro-syntheses. IV. Sima M. Losanitsch (*Ber.*, 1909, 42, 4394—4400. Compare Abstr., 1908, i, 2, 846, 866; ii, 32).—The substances investigated were submitted to the action of the silent electric discharge.

*iso*Pentane absorbs oxygen from the air, and is condensed to a mixture of higher saturated and unsaturated products, in which the latter predominate. *n*-Hexane is more slowly acted on; in this case the saturated products predominate.

Ethyl ether breaks down into formaldehyde, methane, and ethylene. The condensation products C_4H_8O and $C_8H_{14}O_2$ are formed, also ethylal, derived from formaldehyde and ether.

Acetaldehyde is decomposed to the extent of 80%, and condensed to 20% only. The decomposition products are mainly carbon monoxide and methane. The condensation products are polymerides of acetaldehyde and formaldehyde with aldehydic characteristics.

Formic and acetic acids are decomposed. Ethyl acetate gives hydrogen, methane, and carbon monoxide. The condensation products are $C_4H_8O_2$, corresponding with a bimolecular acetaldehyde, $C_5H_{10}O_3$, a combination of formaldehyde and ethyl acetate, and $(C_4H_8O_2)_n$, a higher polymeride of acetaldehyde. Chloroform yields an oil, $C_6H_2Cl_{12}$, and hexachloroethane.

Ethylene yields a volatile product, $C_{16}H_{30}O$, and a non-volatile product, $C_{26}H_{44}O_2$.

Benzene gives a volatile product, $(C_6H_6)_n$, and a non-volatile compound, $C_{24}H_{26}$.

Benzene and hydrogen form a colourless, oily, volatile liquid, $C_{12}H_{14}$, and a non-volatile, red, thick, clear substance, $C_{28}H_{34}$. E. F. A.

Formation of Naphthenes in Mineral Oil. I. Carl Engler (*Ber.*, 1909, 42, 4610—4613).—It is shown conclusively by the author, in conjunction with Routala (compare following abstracts), that olefines, which are formed by the distillation of fats under pressure, when heated under pressure at about 200° readily yield naphthenes and substances closely resembling mineral lubricating oils; consequently, the assumption that the naphthenes in mineral oils owe their origin to the action of a catalyst on olefines is unnecessary (compare Aschan, Abstr., 1902, i, 749). W. H. G.

Formation of Naphthenes. II. Action of Aluminium Chloride on Amylene at Low and Moderately High Temperatures. Carl Engler and O. Routala (*Ber.*, 1909, 42, 4613—4620).—A detailed account of the behaviour of various samples of amylene when treated with aluminium chloride at the ordinary temperature and at about 130°. Generally speaking, the results obtained are in good agreement with those recorded by Aschan (Abstr., 1902, i, 749); thus, the more volatile products are composed mainly of paraffins, such as pentane, *iso*pentane, hexane, $\beta\gamma$-dimethylbutane, γ-methylpentane, heptane, octane, decane, etc., whilst traces of naphthenes are present only in the fractions with high boiling points. W. H. G.

Naphthene Formation. III. Products Formed by Heating Amylene and Hexylene Under Pressure. Carl Engler and O. Routala (*Ber.*, 1909, 42, 4620—4631).—When commercial amylene (β-methyl-Δ^β-butylene) is heated under pressure at 320—325° for thirty-two days, it yields a gas (about 10 litres from 350 grams) and a liquid with a bluish-green fluorescence. The gas is composed of saturated hydrocarbons, paraffins, and polymethylenes, 91·1%; unsaturated hydrocarbons, 1·5%, and hydrogen, 7·4%. The liquid when fractionally distilled yields various paraffins, such as pentane, *iso*pentane, hexane, heptane, and octane, whilst the higher boiling fractions (b. p. 130—250°) consist almost solely of naphthenes identical with, or very similar to, those which have been isolated by Markownikoff and Oglobin from Caucasian petroleum; for example, fractions were obtained having the composition and physical properties of nononaphthene, *iso*decanaphthene, β-decanaphthene, hendecanaphthene, tetradecanaphthene, and pentadecanaphthene; in addition, α-decanaphthene was isolated and identified as the nitro-derivative. The fractions with high b. p.'s closely resemble the mineral lubricating oils.

Δ^β-Hexylene (methylpropylethylene), when heated under pressure at 325° for about thirty days, yields a mixture of gaseous, saturated hydrocarbons, and an oil from which fractions were obtained similar to those derived from amylene. W. H. G.

Chloroethylenes. Karl A. Hofmann and Heinz Kirmreuther (*Ber.*, 1909, 42, 4481—4485).—Whilst ethylene, its homologues and analogues combine rapidly with mercury salts, especially in presence of sodium acetate, di-, tri-, and tetra-chloroethylenes undergo no change under these conditions. With alkaline mercuric cyanide solutions, these haloid derivatives form salt-like, substituted compounds. the ethylene linking remaining intact (compare Abstr., 1908, i, 145); further, they are gradually reduced by platinum chloride, with which ethylene itself combines.

Iodine does not yield additive products with di-, tri-, or tetra-chloroethylene in the dark; with the trichloro-compound a slow action occurs in daylight, but the change is more complicated than simple addition.

The addition of bromine to these haloid derivatives in carbon tetrachloride solution in the dark takes place with measurable velocity (compare Plotnikoff, Abstr., 1906, ii, 12; Herz and Mylius, Abstr., 1907, i, 55; Bauer and Moser, Abstr., 1907, i, 307). With dichloroethylene the value of K calculated for a reaction of the second order is constant ($1{\cdot}18$—$1{\cdot}52.10^{-4}$). With tetrachloroethylene the value of K increases to an approximately constant magnitude, the auto-acceleration of the reaction being due to the catalytic action of an oxidation product, such as carbonyl chloride, the odour of which is observable.

In the case of trichloroethylene the reaction is very complex and irregular. The velocity, which initially is greater than with dichloroethylene, diminishes from $K = 4{\cdot}06 \times 10^{-4}$ to $0{\cdot}58 \times 10^{-4}$, afterwards increasing to the value $2{\cdot}57 \times 10^{-4}$. Here, also, the odour of carbonyl chloride is noticed, and either this compound or an analogous oxidation product doubtless exerts a considerable catalytic influence on the reaction. T. H. P.

Esters of Perchloric Acid. Karl A. Hofmann, [Graf] Armin Zedtwitz, and H. Wagner (*Ber.*, 1909, 42, 4390—4394. Compare Abstr., 1909, ii, 568).—The attempt was made to prepare alkyl esters of perchloric acid by the interaction of nitrosyl perchlorate with alcohols. These perchlorates are formed, but even when very small quantities of substance are used and every precaution is adopted, they are of too explosive a nature to be isolated. The experiments were accordingly restricted to the preparation of esters of ethylene glycol and chlorohydrin, formed by the interaction of ethylene oxide and of epichlorohydrin with perchloric acid, D 1·72, containing sixty-three parts by weight of $HClO_4$.

Chloroperchloratohydrin, $ClO_4{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$, is a colourless, heavy oil. It burns like gun-cotton, explodes when struck more easily than nitroglycerin, but is easily hydrolysed by water and slowly decomposes in moist air. This excludes any practical application as an explosive.

The corresponding *chloronitratohydrin* does not explode, and is hardly hydrolysed at $+17°$ under conditions which cause hydrolysis of more than half of the perchlorate.

Diethylene glycol monoperchlorate, $ClO_4{\cdot}C_2H_4{\cdot}O{\cdot}C_2H_4{\cdot}OH$, is a colour-

less oil, which explodes violently when heated and burns like gun-cotton. It is slightly more stable towards moisture than the chloroperchloratohydrin, but slowly decomposes when exposed to the atmosphere.

E. F. A.

Sodium Alkyl Carbonates. Antoine P. N. Franchimont (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 303—304).—Sodium methyl and ethyl carbonates have been obtained by the action of dry carbon dioxide on the dry sodium alkyl oxide free from alcohol. Both substances are decomposed by water, but not by acetone, or yet when heated to about 180°. Whilst sodium phenyl carbonate is decomposed by acetone, it is shown that the rate of decomposition is greatly reduced if the acetone is dried over phosphoric oxide. H. M. D.

Kephalin. Jakob Parnass (*Biochem. Zeitsch.*, 1909, 22, 411—432).—Kephalin was prepared by extracting the hardened and dried brain with light petroleum. It was separated from the cholesterol and phosphatides by precipitation from this solution by alcohol. From the precipitate thus obtained it was extracted by a small quantity of very cold ether, and thus separated from the cerebrosides. The ratio of P : N in the carefully prepared product is 1 : 1. It readily undergoes hydrolysis with water, acids, and bases. On heating at 120° for twelve hours with barium hydroxide solution, it yields stearic acid, bases, and a barium salt, $C_{27}H_{53}O_{10}PBa_2$, the acid of which is obtained in a yield of about 50% of the kephalin hydrolysed.

On further hydrolysis with alkali, this phosphorus-containing tetrabasic acid yields "kephalinic" or "kephalinolic" acid in a yield equivalent to 18% of the kephalin. This was obtained pure in the form of the *methyl* ester, $C_{19}H_{34}O_2$, which, on treatment with hydrogen, is converted into methyl stearate, m. p. 37°, from which stearic acid, m. p. 69°, was obtained on hydrolysis. The kephalinic acid ester also takes up 1 molecule of oxygen on treatment with air. The free acid obtained from the ester by hydrolysis solidifies on cooling to −8°, but melts on warming to −4°. It boils at 205° in a vacuum, yielding apparently a mixture of free acid and the isomeric lactone. The barium salt, $(C_{18}H_{31}O_2)_2Ba$, is crystalline. The acid can be directly reduced by hydrogen in the presence of palladium to stearic acid. The sodium salt is soluble in ether. The author brings forward reasons for believing that kephalin is constituted differently from the lecithins. S. B. S.

α-Bromopropionic Acid. Ludwig Ramberg (*Annalen*, 1909, 370, 234—239).—I. *l-α-Bromopropionic Acid.*—This acid has been carefully purified by repeated crystallisation and separation of the crystals from the liquid acid by means of a centrifuge; it has m. p. −0·3° to −0·5° (in a sealed capillary tube), D_4^{20} 1·700, D_4^{25} 1·692, $[\alpha]_D^{20}$ −29·0°, $[\alpha]_D^{25}$ −28·5° (compare Abstr., 1906, i, 923). The acid racemises very slowly, the value of $[\alpha]_D^{20}$ changing from −27·0° in May, 1906, to −24·3° in July, 1909.

II. *Inactive α-Bromopropionic Acid.*—A metastable modification of this acid has been obtained by rapidly cooling the liquid acid to −30°; it has m. p. −3·9° (corr.), and is very stable in the absence of the stable variety, but by inoculation changes spontaneously into this acid. The stable form has m. p. 25·7° (corr.), D_4^{20} 1·700 (compare Weinig, Abstr., 1895, i, 16), and is undoubtedly the true racemic form of the acid. W. H. G.

Melting and Solidifying Points of Fatty Substances. I. Binary Mixtures of Stearic, Palmitic, and Oleic Acids. Emilio Carlinfanti and Mario Levi-Malvano (*Gazzetta*, 1909, **39**, ii, 353—375).—The authors discuss the various methods which have been suggested for the determination of the m. p. of fats, and give the results of their investigations on the solidification curves for the systems palmitic-stearic, palmitic-oleic, and stearic-oleic acids.

The solidification diagram for palmitic-stearic acid consists of two curves, the one for the system having for components stearic acid and the additive compound, $C_{16}H_{32}O_2,C_{18}H_{36}O_2$, and the other for the system comprising the additive compound and palmitic acid. The first of these curves, which meets the other at 56°, the crystallisation temperature of the additive compound, is of Roozeboom's type I, and shows neither a maximum nor a minimum, the solidifying point of stearic acid being lowered continuously by addition of the additive compound. The second curve is a combination of Roozeboom's types II and III, and exhibits a maximum at 56·25° and a minimum at 54·75°, neither of these temperatures corresponding with a simple compound of the two components. The additive compound hence forms with palmitic acid three different series of solid solutions.

The diagram for mixtures of stearic and oleic acids is of Roozeboom's type I, the m. p. of stearic acid being depressed at first slowly and afterwards rapidly as the addition of oleic acid is continued. These acids hence form a continuous series of solid solutions (compare Garelli and Montanari, Abstr., 1895, ii, 205). The mixture containing 5% of stearic acid begins to crystallise at 12·4°, after a superfusion of 0·2°, the temperature falling gradually to 7·8°, where a sudden jump to the solidification point of oleic acid takes place, followed by a very slow fall of temperature. This behaviour is explained by the separation at 12·4° of a solid solution, which is richer in stearic acid than the liquid, and does not enter into equilibrium with the liquid, that is, does not absorb oleic acid as the temperature falls. Gottlieb (*Annalen*, 1846, **57**, 37) gave for oleic acid the m. p. 14° and the solidifying point 4°; for their oleic acid, which gave an iodine number of 90·5 instead of the theoretical 90, the authors found the solidifying point 9° with 2·5° superfusion.

The system comprising palmitic and oleic acids exhibits behaviour similar to that of stearic and oleic acids.

The additive compound formed by palmitic and stearic acids probably represents the original margaric acid, the more recent daturic acid, and, possibly, the synthetic margaric acid assumed to exist at the present day. T. H. P.

Melting and Solidifying Points of Fatty Substances. II. Ternary Mixtures of Palmitic, Stearic, and Oleic Acids. Emilio Carlinfanti and Mario Levi-Malvano (*Gazzetta*, 1909, **39**, ii, 375—385. Compare preceding abstract).—In order to obtain data for the determination of the proportions of palmitic, stearic, and oleic acids in a mixture of the three, the authors have investigated the solidifying points of fifty mixtures of the three acids.

With each mixture, the temperature falls regularly while the mixture remains liquid, rises 1—1·5° when crystallisation commences, then again falls slowly until crystallisation is complete, and subsequently more rapidly. In no case is an arrest of the temperature observed during the fall, so that the solid formed by the crystallisation of any one mixture of the acids is formed of a single phase, composed of solid solutions of the three acids, the miscibility of these in the solid state being complete. The results are given in the form of an equilateral triangle diagram. Each temperature of solidification is common to a series of mixtures, both of the three acids and of two of them, and, in order to determine whether a mixture under examination consists of two or three acids, and to ascertain the proportions of each, it is necessary either to estimate the stearic acid by Hehner and Mitchell's method, or to determine the iodine number. It is found that the iodine number corresponds very closely with the proportion of oleic acid in the mixture. The iodine numbers and the temperatures at which crystallisation commences are given for a number of mixtures of fatty acids derived from natural fats and oils.

T. H. P.

Hydrolysis of Fats and Oils. Rudolf Wegscheider (*Chem. Zeit.*, 1909, **33**, 1220).—Some remarks on Kellner's paper (Abstr., 1909, i, 759).

Kellner's observations are in harmony with the theory of a gradual saponification. L. de K.

Detergent Action of Soap Solutions. Part II. Walthère Spring (*Rec. trav. chim.*, 1909, **28**, 424—443).—In the previous paper of this series (Abstr., 1909, i, 628) the detergent action of soap solutions for lampblack was considered, and in the present paper the investigation is extended to ferric compounds, and more especially "red ochre." The conclusions as to the general mode of action of soap, already indicated, are confirmed.

The red ochre employed had the composition represented by the formula $7Fe_2O_3,3H_2O$. As in the case of lampblack, so with ochre (*loc. cit.*), an *optimum* concentration of soap solution exists, from which the rate of deposition of the ochre is a minimum. This concentration is about 0·5%. The colloidal compound formed between soap and ochre is slightly soluble in water, so that all the solutions used retained a red colour even after the deposition of the ochre. Evidence as to the formation of this colloidal compound was obtained by analysis of soap solutions in water or methyl alcohol, in which ochre had been suspended. The ashes from these were less in amount than those from the original soap solutions, showing that a portion of

the soap had been carried out by the ochre. It appears, therefore, that, as with lampblack, the soap is decomposed into a basic portion and an acid portion, the former being carried down by the ochre. The deposition of ochre from suspension in water is accelerated by alkalis or acids so long as more than 0·078% of alkali or more than 0·0001% of acid is present.

Water containing ochre in suspension may be filtered clear eventually by passing it many times through filter paper, but the ochre deposited in such filter paper is again carried through by soap solution. The amount of ochre thus carried through by soap solution does not increase with the concentration of the latter until this falls below 0·25%.

Soap solutions tend to flocculate colloidal solutions of ferric hydroxide, and a minimum molecular concentration (1 mol. soap to 2·16 mols. of ferric oxide) exists, at which turbidity but no precipitation occurs, and a maximum concentration (1 mol. soap to 3·47 mols. of ferric oxide), at and beyond which complete flocculation of the ferric compound takes place. The precipitate formed is yellow in colour, but on drying becomes chocolate-brown, and is a colloidal compound of soap and ferric hydroxide having the formula

$$38Fe_2O_2,9(NaC_{17}H_{33}O_2),71H_2O.$$

It does not adhere to glass, paper, or skin, and is quite different in properties from "ferric soap" prepared in the usual way by double decomposition. The results indicate that the detergent property of soap for ferric hydroxide is due to the formation of a colloidal compound of the two substances, which no longer has the property of adhering to fabrics or tissues. T. A. H.

Hydroxyaliphatic Acids from the Products of the Interaction of Hypochlorous Acid or Chlorine and the Glycerides of Aliphatic Acids of Animal or Vegetable Origin. Georges Imbert and Consortium für Elektrochemische Industrie (D.R.-P. 214154. Compare Abstr., 1909, i, 875).—Instead of preparing the dihydroxyaliphatic acids from the product of the action of chlorine or hypochlorous acid on the fatty acids themselves, their glycerides may be employed, and the hydrolysis of the dichloro- or chlorohydroxyglyceride can be effected at the same time as the replacement of chlorine by hydroxyl.

The glyceride of chlorohydroxystearic acid, obtained by the action of hypochlorous acid on olive oil, was heated with a 7% solution of sodium carbonate at 150°, and the dihydroxystearic acid precipitated with sulphuric acid.

The glyceride of dichlorostearic acid, produced by the action of chlorine on olive oil, is hydrolysed in the same way. F. M. G. M.

Stereochemistry of the Glutaconic Acid Group. Franz Feist (*Annalen*, 1909, **370**, 41—60. Compare Perkin, Trans., 1897, 71, 1182; 1902, **81**, 246; 1903, **83**, 8, 771).—A theoretical paper devoted to a discussion of the stereoisomerism of alkyl derivatives of glutaconic acid and of the observations recorded in the following abstracts and p. i, 39.

It is found that α-methylglutaconic acid in analogy to β-methylglutaconic acid (compare Feist, Abstr., 1906, i, 334) exists in two stereoisomeric modifications, thus providing another case against the view advanced by Thorpe (Trans., 1905, 87, 1669). Attempts to prepare two isomeric β-phenylglutaconic acids have been unsuccessful.

Many alkyl derivatives of glutaconic acid have been isolated in one form only, and in cases where the anhydride has been prepared, as, for example, the αγ-dimethyl, β-methyl-α-ethyl, and αβγ-trimethyl derivatives, these compounds have been regarded as the *cis*-modifications. The great stability of these compounds and the impossibility of converting them into the more stable *trans*-isomerides made it appear probable that, notwithstanding the close relationship existing between the acid and its anhydride, the acid might be the *trans*-form produced by the spontaneous transformation of the *cis*-isomeride at the moment of its production from the anhydride. Attempts were made, therefore, to prevent the transformation of the *cis*-compound into the *trans*-form by acting on the anhydride with alkali in the presence of an anti-catalyst, and with success; for example, the anhydride of α-methylglutaconic acid when treated with alkali in the presence of casein and subsequently with silver nitrate yields a silver salt, which, when decomposed by hydrogen sulphide, gives the *cis*-acid, m. p. 118°; in the absence of casein, the *trans*-acid, m. p. 145—146°, containing traces of the *cis*-isomeride, is obtained.

The effect on the stability of the stereo-isomerides produced by the replacement of the various hydrogen atoms of glutaconic acid by alkyl groups may be summarised as follows: (1) Replacement of the two α-hydrogen atoms renders the isomerides very stable; they cannot be converted one into the other; if only one atom is substituted, then the isomerides may with difficulty be transformed one into the other. The effect of alkyl groups in the α-position is neutralised to some extent by substitution of a β- or γ-hydrogen atom; thus, *cis*-aαγ-trimethylglutaconic acid passes quite readily into the *trans*-acid. (2) The compounds obtained by replacing a β- or γ-hydrogen atom by an alkyl group, even if one of the α-hydrogen atoms is likewise replaced by an alkyl group, have been obtained only in the stable *trans*-form, with the exception of β-methylglutaconic acid (compare Perkin, Trans., 1902, 81, 246; Thorpe, Trans., 1905, 87, 1669; Perkin and Thorpe, Trans., 1898, 71, 1182).

The readiness with which the glutaconic acids yield anhydrides depends largely on the position of the alkyl groups; in agreement with the results of Victor Meyer and of Auwers, the tendency to form an anhydride is increased by the accumulation of alkyl groups, but it is found that substitution of the β-hydrogen atom leads more particularly to the ready formation of anhydrides; thus, αβγ-trimethylglutaconic acid, αβ-dimethylglutaconic acid, β-phenylglutaconic acid, and β-methylglutaconic acid yield anhydrides when fused, whereas αγ-dimethylglutaconic acid and α-methylglutaconic acid do not yield anhydrides when treated similarly.

The stability of the anhydrides towards the addition of water, likewise the ability of the various glutaconic acids to form additive

products, depends largely on the position of the alkyl group, but rules of general applicability cannot be given. W. H. G.

Stereoisomeric α-Methylglutaconic Acids. Franz Feist and G. Pomme (*Annalen*, 1909, **370**, 61—72. Compare preceding abstract). —Ethyl sodiodicarboxyglutaconate when treated with an alcoholic solution of methyl sulphate yields ethyl dicarboxymethylglutaconate, which, when hydrolysed with aqueous alkali or hydrochloric acid, yields a mixture of two isomeric α-methylglutaconic acids, melting at 145—146° and 118° respectively. The acid m. p. 145—146°, first described by Conrad and Guthzeit, is shown to be the *trans*-modification, since α-methylglutaconic anhydride absorbs water from the air, yielding the acid, m. p. 118°, and when treated with alkali in the presence of casein yields the same acid, m. p. 118°; the crystalline *calcium* ($2\frac{1}{2}H_2O$) and *barium* ($2H_2O$) salts were analysed; the acid changes partly into the *cis*-isomeride when treated with dilute hydrochloric acid or aqueous sodium hydroxide.

cis-α-*Methylglutaconic acid*, $C_6H_8O_4$, m. p. 118°, does not alter when fused, but is partly converted into the *trans*-isomeride by hot dilute hydrochloric acid; the *barium* ($2H_2O$) and *calcium* ($4H_2O$) salts were analysed.

α-*Methylglutaconic anhydride*, $C_6H_6O_3$, cannot be prepared by the action of acetyl chloride or thionyl chloride on the acid, but is obtained by treating the acid with phosphorus pentachloride; it crystallises in long needles, m. p. 85°, and when warmed with aniline yields the *semianilide*, $CO_2H{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO{\cdot}NHPh$ or $CO_2H{\cdot}CH{:}CH{\cdot}CHMe{\cdot}CO{\cdot}NHPh$, crystallising in white needles, m. p. 165°.

trans α-Methylglutaconic acid interacts (1) with aniline at 150°, yielding α-*methylglutaconanil*, $CH\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}CHMe{\cdot}CO\\ CH\text{——}CO\end{matrix}>NPh$, which crystallises in needles, m. p. 229°, and (2) with hydrobromic acid in glacial acetic acid, with the formation of *bromo-α-methylglutaconic acid*, $C_6H_9O_4Br$, crystallising in needles, m. p. 141°.

An attempt to prepare α-methylglutaconic acid by reducing ethyl methylacetonedicarboxylate, heating the product with acetic anhydride, and hydrolysing the ester so formed, led to the isolation of a *substance*, $C_{11}H_{14}O_6$, m. p. 141°. W. H. G.

αγ-Dimethylglutaconic Acids. Franz Feist and R. Reuter (*Annalen*, 1909, **370**, 82—92. Compare preceding abstracts; Reformatzky, Abstr., 1899, i, 481; Blaise, Abstr., 1903, i, 400, 548). —The object of this investigation was to prepare a second αγ-dimethylglutaconic acid by making use of casein as an anti-catalyst; this could not be done, however, owing to the impossibility of preparing a normal anhydride of the acid. αγ-Dimethylglutaconic acid does not pass into the anhydride when fused or when heated with acetyl chloride, thionyl chloride, or concentrated sulphuric acid. When warmed with phosphorus pentachloride it yields small quantities of a

substance, $CH\ll^{CMe-CO}_{CMe\cdot CCl}\gg O$ (?), crystallising in small needles, m. p. 82—83°, and relatively large quantities of a *substance*, the properties of which are most in accord with the formula

$$CH\ll^{CMe—CO\cdot C(:CMe—CO)}_{CHMe\cdot CO\cdot CMe\cdot CO\cdot O}$$

The latter substance forms white crystals, m. p. 207—208°, and undergoes the following changes: (1) when boiled with water it yields the dibasic *acid*, $C_{14}H_{16}O_6$, m. p. 176—176·5° (decomp.); (2) when treated with aniline, it yields the *semianilide*, $CO_2H\cdot C_{12}H_{14}O_2\cdot CO\cdot NHPh$, m. p. 247—248°, and a *substance*, m. p. 151°, obtained as a white powder; (3) it is converted by a solution of sodium methoxide in methyl alcohol into the *methyl hydrogen* ester,

$$CO_2H\cdot C_{12}H_{14}O_2\cdot CO_2Me,$$

a white, crystalline substance, m. p. 183—183·5°, and a crystalline *substance*, $C_{15}H_{20}O_4$, m. p. 142—143°; (4) it combines with bromine, yielding a *dibromo*-derivative, $C_{14}H_{14}O_5Br_2$, m. p. 163°. W. H. G.

Derivatives of Propylsuccinic Acid. René Locquin (*Bull. Soc. chim.*, 1909, [iv], 5, 1071—1074).—Propylsuccinic acid (m. p. 91—92°) was prepared by Waltz's process (Abstr., 1882, 948), and converted into the anhydride, b. p. 145—150°/13 mm., by heating it, complete transformation being secured by boiling the product with acetic anhydride. The following new derivatives suitable for the identification of the acid are described.

With aniline the anhydride yields the *monoanilide*, m. p. 123—126°, which crystallises from benzene on adding alcohol, and on heating at 180—200° during fifteen minutes passes into the *anil*, m. p. 83°, which crystallises from a mixture of alcohol and light petroleum.

Ethyl propylsuccinate has b. p. 132—134°/25 mm. The methyl ester, b. p. 107°/11 mm. or 112°/15 mm., on treatment with ammonia yields the *diamide*, m. p. 234—235°, which crystallises in colourless needles from alcohol containing acetic acid. With hydrazine hydrate the methyl ester yields the *dihydrazide*, m. p. 176°, which separates from alcohol as a white powder, and condenses with benzaldehyde to give a *dibenzylidene* derivative, m. p. 226°, a white powder, which is difficult to purify by reason of its insolubility in organic solvents.

T. A. H.

Cholic Acid. I. Martin Schenck (*Zeitsch. physiol. Chem.*, 1909, 63, 308—312).—When an alkaline solution of dehydrocholic acid (Hammarsten, Abstr., 1881, 624; Mylius, *ibid.*, 1886, 952; 1887, 983) is reduced electrolytically, using lead terminals and a porous cell, the chief product is *reductodehydrocholic acid*, $C_{24}H_{36}O_5$, a compound intermediate between cholic and dehydrocholic acids. The acid crystallises from benzene in minute, colourless needles, m. p. 188°, and yields a *dioxime*, $C_{24}H_{36}O_3(NOH)_2$, which crystallises from alcohol in slender needles decomposing at 254—256°. J. J. S.

American Colophony. Paul Levy (*Ber.*, 1909, 42, 4305—4308). —When sodium abietate from American colophony is oxidised with a 2% solution of potassium permanganate at the ordinary temperature, the products are *tetrahydroxyabietic acid*, propionic acid, *iso*butyric acid, and resins. The tetrahydroxy-derivative, $C_{20}H_{34}O_6$, is separated from the resins by treatment with acetone, when it forms a colourless powder, which crystallises in well-developed crystals, m. p. 246—247° (decomp.). The *silver* salt, $C_{20}H_{33}O_6Ag,2{\cdot}5H_2O$, and *barium* salt,

$$C_{40}H_{66}O_{12}Ba,4H_2O,$$

are described.

The tetrahydroxy-acid is probably identical with Fahrion's tetrahydroxysylvic acid (Abstr., 1901, i, 166), and the formation of the acid is regarded as supporting the author's view that abietic acid contains two ethylene linkings. J. J. S.

Catalytic Preparation of Unsymmetrical Aliphatic Ketones. Jean B. Senderens (*Compt. rend.*, 1909, 149, 995—997. Compare Abstr., 1909, i, 286, 627).—The method for the preparation of symmetrical ketones already described has now been extended to the production of mixed ketones; thus methyl ethyl ketone is obtained by passing a mixture of the vapours of acetic and propionic acids over thorium dioxide at 400—430°. Acetophenone and acetone are obtained when acetic acid (3 mols.) and benzoic acid (1 mol.) are employed. The separation of the unsymmetrical ketones from the accompanying smaller quantities of symmetrical products is easily effected by fractionation. W. O. W.

Synthesis of Ketones by means of Organo-magnesium Compounds. Julius Salkind and (Madame) T. Beburischwili (*Ber.*, 1909, 42, 4500—4502).—The diminution of the reactivity of the carboxyl group towards organo-magnesium compounds, produced by a second carboxyl group (compare Simonis and Arand, Abstr., 1909, i, 932), probably accounts for the formation of esters of β-keto-acids by the action of magnesium on esters of α-bromo-acids (compare Abstr., 1907, i, 22; Zeltner and Reformatsky, Abstr., 1907, i, 23; Salkind and Baskoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 327). In this case the magnesium compound, $MgBr{\cdot}CHR{\cdot}CO_2Et$, formed in the ordinary way, condenses immediately with its own carboxyl group, yielding a product of the formula: $MgBr{\cdot}CHR{\cdot}C(OEt)(OMgBr){\cdot}CHR{\cdot}CO_2Et$, which gives a good yield of a substituted acetoacetic ester when decomposed by means of water. Tertiary hydroxy-acids are never obtained in this way, so that with them, addition of a second molecule of the Grignard compound does not occur.

The authors have investigated the action of Grignard's compounds on the sodium salts of carboxylic acids (compare Grignard, Abstr., 1904, i, 213; Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1906, i, 660). When perfectly dry sodium acetate or propionate is added, with cooling and continual stirring, to the calculated proportion of the organo-magnesium compound, and the mixture decomposed after twenty-four hours by iced water, the ketone is obtained, the yield of crude product being 25—27%. Thus, with magnesium *iso*-

butyl bromide and sodium acetate, methyl *iso*butyl ketone is obtained; with magnesium *iso*amyl iodide and sodium acetate, methyl *iso*amyl ketone; with magnesium phenyl bromide and sodium acetate, acetophenone; and with magnesium ethyl bromide and sodium propionate, diethyl ketone. T. H. P.

The Hexosephosphate Formed by Yeast-Juice from Hexose and a Phosphate. William J. Young (*Proc. Roy. Soc.*, 1909, *B*, 81, 528—545. Compare Abstr., 1905, ii, 109; 1906, i, 470; 1908, ii, 590; 1909, i, 863).—The compound formed during the accelerated fermentation of dextrose, lævulose, and mannose by yeast-juice in the presence of a soluble phosphate is a salt of an acid which probably has the formula $C_6H_{10}O_4(PO_4H_2)_2$, and may be isolated by precipitation of its lead salt. The free acid may be obtained in solution by decomposing this lead salt with hydrogen sulphide. The acid is very unstable, and readily decomposes on keeping, or on evaporating even at the ordinary temperature in a vacuum over sulphuric acid, with formation of a reducing substance and phosphoric acid. It reduces Fehling's solution, but no osazones or hydrazones have been obtained from it. No differences have been detected between the hexosephosphoric acids or their salts, whether derived from dextrose, lævulose, or mannose. The salts of lead, barium, silver, and cadmium have been prepared. G. S. W.

Platinum. Alexander Gutbier and Fr. Bauriedel (*Ber.*, 1909, 42, 4243—4249. Compare Abstr., 1903, ii, 488).—In connexion with the revision of the atomic weight of platinum, the authors have prepared a number of substituted ammonium salts of hydrogen platinibromide. A solution of hydrogen platinichloride was evaporated on the water-bath six times with concentrated hydrobromic acid. The residue was then treated several times in a similar manner with hydrobromic acid containing bromine, and the final residue dissolved in dilute hydrobromic acid. In this way a dark carmine-red solution was obtained, from which crystals of hydrogen platinibromide, $H_2PtBr_6,9H_2O$, separated on evaporation over lime. By the addition of solutions of substituted ammonium bromides to this solution, the following platinibromides were precipitated in a pure condition.

Methylammonium platinibromide, $(NH_3Me)_2PtBr_6$: light brown to reddish-brown, six-sided, regular plates, which are still solid at 260°.

Dimethylammonium platinibromide, $(NH_2Me_2)_2PtBr_6$: slender, red, rhombic prisms, m. p. 232° (decomp.). *Trimethylammonium platinibromide*, $(NHMe_3)_2PtBr_6$: dark red octa- and hexa-hedra, m. p. 253—254° (decomp.). *Ethylammonium platinibromide*, $(NH_3Et)_2PtBr_6$: yellowish-red, six-sided, regular plates, which are still solid at 264°. *Diethylammonium platinibromide*, $(NH_2Et_2)_2PtBr_6$, monoclinic plates, m. p. 251—252° (decomp.). *Triethylammonium platinibromide*, $(NHEt_3)_2PtBr_6$: ruby-red crystals, probably monoclinic, m. p. 231—232°. n-*Propylammonium platinibromide*, $(NH_3Pr^{\alpha})_2PtBr_6$, red, monoclinic plates, m. p. 257—258° (decomp.). iso*Propylammonium platinibromide*, $(NH_3Pr^{\beta})_2PtBr_6$: yellowish-red, six-sided plates, m. p.

267°. *n-Butylammonium platinibromide*, $(C_4H_9\cdot NH_3)_2PtBr_6$: yellowish-red, six-sided plates, m. p. 256°. iso*Butylammonium platinibromide*, $(C_4H_9\cdot NH_3)_2PtBr_6$: ruby-red, monoclinic prisms, m. p. 266°. *Ethylenediammonium platinibromide*, $C_2H_{10}N_2PtBr_6$: red, six-sided prisms, which remain solid at 270°. *Propylenediammonium platinibromide*, $C_3H_{12}N_2PtBr_6$: dark red prisms, which are still solid at 270°.

T. S. P.

Preparation of Hydroxamic Acids from Hydroxylamine Salts of Organic Acids. Lauder William Jones and Ralph Oesper (*Amer. Chem. J.*, 1909, 42, 515—520).—When hydroxylamine formate (Sabenéeff, Abstr., 1900, ii, 14), m. p. 76°, is left for several weeks at the ordinary temperature, or heated for a few minutes at its m. p., it is partly converted into formhydroxamic acid. If, however, the salt is heated above 80°, violent decomposition occurs. The reaction is reversible, and it is shown that formhydroxamic acid can be synthesised by treating hydroxylamine with dry carbon monoxide. When hydroxylamine acetate is heated at 90° in a sealed tube, acethydroxamic acid is produced in a yield of about 25—30%. Preliminary experiments have shown that hydroxylamine benzoate and anisate also yield the corresponding hydroxamic acids when heated slightly above their m. p.'s. E. G.

Reaction between Hydrogen Sulphide and Cyanaminodithiocarbonates. Arthur Rosenheim (*Ber.*, 1909, 42, 4439—4440). —Polemical. A reply to Hantzsch (Abstr., 1909, i, 894; compare Rosenheim, Levy, and Grünbaum, *ibid.*, i, 776). R. V. S.

Dithiourethanes. II. Preparation of Thioglycols from Bisdithiourethanes. Julius von Braun (*Ber.*, 1909, 43, 4568—4574. Compare Abstr., 1902, i, 271).—The behaviour of dihalogen substituted aliphatic hydrocarbons towards dithiocarbamates has been studied to test the influence of the distance between the halogens on the introduction of the thiourethane complex. The reaction between $\omega\omega'$-di-iodo-ethane, -propane, -butane, -pentane, -hexane, and -decane and a dithiocarbamate takes place readily and with equal velocity at both ends of the molecule, forming only bisdithiourethanes, $NR_2\cdot CS\cdot S\cdot[CH_2]_x\cdot S\cdot CS\cdot NR_2$, and never iododithiourethanes,

$$NR_2\cdot CS\cdot S\cdot[CH_2]_x\cdot I.$$

The products are indifferent substances; the *piperidine* derivatives, $C_5NH_{10}\cdot CS\cdot S\cdot[CH_2]_x\cdot S\cdot CS\cdot C_5NH_{10}$, have been analysed. They crystallise remarkably well, and the melting point only slowly falls with an increase in the length of the chain. The *propane* derivative has m. p. 140°; *butane* derivative, m. p. 125°; *pentane* derivative, m. p. 103°; *hexane* derivative, m. p. 94°; *decane* derivative, m. p. 90°.

The di-iodo-compounds interact similarly with carbon disulphide and primary amines, but the dithiourethanes formed are more soluble, and were only obtained as viscid oils which decompose when warmed.

On mixing finely powdered ammonium dithiocarbamate with the di-iodo-compounds in alcoholic solution, a colourless precipitate

gradually forms; the time of formation of this does not seem to depend on the molecular weight of the iodide. The bisdithiourethanes formed were not obtained quite pure, and did not show sharp melting points. They softened from 100° to 150°. When warmed with potassium hydroxide, they are converted into the corresponding thioglycols.

Butylene αδ-dithiol, $HS\cdot[CH_2]_4\cdot SH$, is a colourless oil, b. p. 105—106°/30 mm.; the *benzoyl* derivative forms long needles, m. p. 49°.

Hexylene aζ-dithiol, $HS\cdot[CH_2]_6\cdot SH$, has b. p. 118—119°/15 mm.; the *benzoate* has m. p. 57°.

Decalene ακ-*dithiol* has b. p. 176°/16 mm., m. p. 20°; the *benzoate* has m. p. 55°. It is almost without odour. E. F. A.

Compounds from Guanylcarbamide and Diguanide. Julius Söll and Albert Stutzer (*Ber.*, 1909, **43**, 4532—4541).—On evaporating dicyanodiamide with mineral acids, salts of guanylcarbamide are obtained, from which the free base has been prepared. To prepare dicyanodiamide, crude commercial cyanamide is stirred to a paste with water, boiled, and filtered hot; the dicyanodiamide crystallises from the filtrate. When evaporated with sulphuric acid, *guanylcarbamide hydrogen sulphate*, $NH{:}C(NH_2)\cdot NH\cdot CO\cdot NH_2,H_2SO_4$, is formed, which when decomposed with barium hydroxide gives guanylcarbamide. This crystallises from alcohol $+C_2H_6O$ in lustrous, glass-like prisms, which very rapidly take up carbon dioxide from the air. The alcohol evaporates in a desiccator. The free base has m. p. 105°; it evolves ammonia at 160°, or on boiling with water. The *picrate* crystallises in yellow plates, m. p. 265° to a clouded, yellow mass, decomp. 285°; it may be used to estimate guanylcarbamide quantitatively. The heat of combustion of guanylcarbamide nitrate is 327·4 Cal. Guanylcarbamide condenses readily in alcoholic solution, forming pyrimidine bases.

Guanylcarbamidesulphonic acid, $C_2H_5ON_4\cdot SO_3H$, is obtained by heating guanylcarbamide sulphate with acetic anhydride; it crystallises in prisms, decomp. 220—230°; the *ammonium* salt forms short, thick prisms, m. p. 165—167°; the *barium* and *calcium* salts are similar. Acetic anhydride and sulphuric acid convert the sulphonic acid into acetylguanylcarbamide.

Acetylsulphuric acid acts on acetanilide to form acetylsulphanilic acid, crystallising in long needles from acetic acid (compare Schröter, Abstr., 1906, i, 415).

Guanylcarbamide condenses with monochloroacetic acid on heating to guaninoacetic acid (Ramsay, Abstr., 1909, i, 88). It forms a picrate crystallising in plates, m. p. 235—237°, differing from that described by Ramsay, m. p. 201° (*loc. cit.*). The new guaninoacetic acid is probably bimolecular; when boiled with hydrogen chloride, the hydrochloride of unimolecular guaninoacetic acid is formed, which gives the picrate, m. p. 202°. E. F. A.

Action of Hydrogen Chloride on Acetone Cyanohydrin. A. J. Ultée (*Rec. trav. chim.*, 1909, **28**, 349—353. Compare Pinner, Abstr., 1884, 1292).—When dry hydrogen chloride is passed into

acetone cyanohydrin, cooled to 0°, two condensation products are formed.

The first of these is an *imino-ether hydrochloride*,

$$C_8H_{14}O_2N_2,HCl,H_2O,$$

m. p. 231° (decomp.), and remains undissolved when the reaction product is mixed with rather less than its own volume of water. It is readily soluble in water, is precipitated therefrom by hydrochloric acid, and, on addition of alkalis, yields the *imino-ether*, which does not melt even at 280°, and on boiling with excess of alkali dissolves with evolution of ammonia, but, unlike most substances of this class, is not decomposed by water. The formula $HO\cdot CMe_2\cdot C(NH)\cdot O\cdot CMe_2\cdot CN$ or $HN{:}C\langle^{O\cdot CMe_2}_{CMe_2\cdot O}\rangle C{:}NH$ is provisionally assigned to this substance.

The second *product*, $C_{12}H_{19}O_5N$, m. p. 193°, separates almost at once in colourless crystals from that part of the reaction mixture which is miscible with water. It is slightly soluble in water, readily so in chloroform, acetone, or alkalis, but is precipitated from solutions in alkalis by acids. When boiled with alkalis, it evolves ammonia, and on long boiling with hydrochloric acid forms *α-iso*butyric acid. The following formula is provisionally assigned to this product:

$$\begin{matrix} O\text{—}CMe_2\cdot CO\cdot NH \\ | \\ CMe_2\cdot CO\cdot O\cdot CMe_2 \end{matrix}\rangle CO.$$

T. A. H.

Constitution and Behaviour of Semicarbazidesemicarbazones. Hans Rupe and Sidonius Kessler (*Ber.*, 1909, **42**, 4503—4510).—Mesityl oxide semicarbazidesemicarbazone,

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CMe_2\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

obtained in the form of the hydrochloride by the gradual action of semicarbazide hydrochloride on mesityl oxide, is stable in dilute aqueous alkalis, giving solutions which reduce ammoniacal silver nitrate and Fehling's solutions; the *hydrochloride*, $C_8H_{19}O_2N_6Cl$, forms microscopic, white needles, m. p. 211—212° (decomp.).

When a solution of the above semicarbazidesemicarbazone in dilute hydrochloric acid is treated with benzaldehyde, the semicarbazide residue united by a double linking to the carbon atom of the ketonic group is removed and benzaldehydesemicarbazone formed, together with diacetonesemicarbazide, $NH_2\cdot CO\cdot NH\cdot NH\cdot CMe_2\cdot CH_2\cdot COMe$, which can be separated as a nitroso-derivative. If the aqueous solution containing diacetonesemicarbazide hydrochloride is left for some time and then extracted with ether, the latter contains the compound obtained (1) by Scholtz (Abstr., 1896, i, 343) by distilling mesityl oxide semicarbazone; (2) by Harries and Kaiser (Abstr., 1899, i, 637) by the direct action of semicarbazide hydrochloride on mesityl oxide, and (3) by Rupe and Schlochoff (Abstr., 1904, i, 144) by boiling mesityl oxide semicarbazidecarbazone with water. This compound, m. p. 131°, being formed from diacetonesemicarbazide, cannot be represented by the first of the two formulæ given by Harries and Kaiser (*loc. cit.*), although the evidence is insufficient to establish the accuracy of the second formula. In aqueous solution the compound reduces gold chloride in the cold and ammoniacal silver solution on

heating; by 10—15% sodium hydroxide solution it is only slowly and sparingly decomposed, with evolution of ammonia, and boiling with acids does not result in the removal of a $\cdot CO\cdot NH_2$ group. With nitrous acid, it yields mesityl oxide and carbamineazoimide (Thiele and Stange, Abstr., 1895, i, 252), which can arise only from a semicarbazone or from free semicarbazide, so that the ring-compound would appear to have been first resolved.

Nitrosodiacetonesemicarbazide,

$$NH_2\cdot CO\cdot NH\cdot N(NO)\cdot CMe_2\cdot CH_2\cdot COMe,$$

prepared by the action of nitrous acid on diacetonesemicarbazide, or, together with carbamineazoimide, by the action of nitrous acid (2 mols.) on mesityl oxide semicarbazidesemicarbazone (1 mol.), forms white, rectangular plates, m. p. 145—146° (decomp.), gives Liebermann's reaction, is partly decomposed by water or mineral acids, forming azoimide, and when heated above its m. p. yields nitrogen, nitric oxide, carbon dioxide, ammonia, and azoimide. With semicarbazide (1 mol.) it gives *nitrosodiacetonesemicarbazidesemicarbazone*, $NH_2\cdot CO\cdot NH\cdot N(NO)\cdot CMe_2\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2$, which forms small, white needles, m. p. 158°. By alkali in the cold, nitrosodiacetonesemicarbazide is slowly decomposed according to the scheme:

$$\begin{matrix} CMe_2\cdot CH_2\cdot COMe \\ | \\ NO\cdot N\cdot NH\cdot CO\cdot NH_2 \end{matrix} = CMe_2{:}CHAc + NO\cdot NH\cdot NH\cdot CO\cdot NH_2 \longrightarrow$$

$$\begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!N\cdot CO\cdot NH_2 + H_2O \longrightarrow N_3H + CO_2 + NH_3.$$

When nitrosodiacetonesemicarbazide is dissolved in concentrated hydrochloric acid, acetic acid, 40% phosphoric acid, or acetic anhydride, and the solution subsequently diluted and treated with semicarbazide hydrochloride and potassium acetate, a *compound*, $C_6H_{11}O_2N_4$, forming aggregates of slender needles, m. p. 172°, is obtained, which is decomposed by water or dilute sulphuric acid, giving azoimide, and by dilute hydrochloric acid, yielding benzaldehydesemicarbazone. T. H. P.

Metallic Derivatives of Chloro- and Bromo-acetylene. Karl A. Hofmann and Heinz Kirmreuther (*Ber.*, 1909, **42**, 4232—4238. Compare Abstr., 1908, i, 145).—Mercury tribromoethylene, $Hg(CBr{:}CBr_2)_2$, crystallises in well-developed monoclinic prisms [$a : b : c = 1{\cdot}4829 : 1 : 0{\cdot}5637$; $\beta = 105°26'$].

Mercury chloroacetylide, $Hg(C{:}CCl)_2$, obtained by shaking *s*-dichloroethylene with mercuric cyanide and aqueous potassium hydroxide solution, crystallises in thin, quadratic plates. The crystals exhibit strong double refraction, and decompose at 195°. When mixed with an ethereal solution of iodine and exposed to sunlight, the mercury compound yields *chlorotri-iodoethylene*, $CClI{:}CI_2$, which crystallises in long plates, m. p. 78—80°.

Mercury bromoacetylide, $Hg(C{:}CBr)_2$, can be prepared from dibromoethylene and an alkaline solution of mercuric cyanide, or by passing the gases, obtained by the action of alcoholic potassium hydroxide on tribromoethylene, into an alkaline solution of mercuric cyanide. It crystallises in thin, rectangular plates, which decompose at 153—155°, and detonate when rubbed on a porous plate. It is volatile

in steam, and is decomposed by boiling with dilute hydrochloric acid or potassium cyanide solution, yielding bromoacetylene. It readily forms an additive compound with mercuric bromide in the form of an amorphous powder. Pure chloro- and bromo-acetylene are readily prepared by warming the respective mercury compounds with potassium cyanide solution, care being taken that the air in the apparatus is replaced by hydrogen. When chloroacetylene is passed into ammoniacal silver nitrate solution, a white precipitate of AgC:CCl is formed. This darkens rapidly on exposure to sunlight, and is more explosive than silver acetylide. The corresponding explosive copper derivative has also been prepared.

Chloroacetylene mixed with hydrogen reacts with a saturated aqueous solution of mercuric chloride, yielding *trichloromercuriacetic acid*, $C(HgCl)_3 \cdot CO_2H$ (compare Abstr., 1905, i, 2), in the form of a crystalline powder, which is decomposed by hydrochloric acid, forming mercuric chloride and acetic acid. The acid dissolves in cold dilute potassium hydroxide solution, but, when heated, polymeric mercuriacetic acid is precipitated. When chloroacetylene is led into a solution of mercuric chloride and sodium acetate, a precipitate of *dichloromonohydroxytrimercuriacetic acid*, $OH \cdot Hg \cdot C(HgCl)_2 \cdot CO_2H$, is obtained. When dissolved in cold dilute potassium hydroxide solution and precipitated with carbon dioxide, *tri-hydroxymercuriacetic acid*,

$$C(Hg \cdot OH)_3 \cdot CO_2H,$$

is obtained as a yellowish-white powder.

When mercury chloroacetylide is shaken with a solution of mercuric chloride and sodium acetate, a *precipitate*, $C_4H_2O_2Cl_4Hg_3$, is thrown down. J. J. S.

Halogen-amino-acids. VI. Iodo-derivatives of *p*-Toluidine. 3 : 5-Di-iodo-4-aminobenzoic Acid. Henry L. Wheeler and Leonard M. Liddle (*Amer. Chem. J.*, 1909, 42, 441—461).—The only iodo-derivatives of *p*-toluidine hitherto described are the 2-iodo-derivative (Willgerodt and Gartner, Abstr., 1908, i, 876) and a di-iodo-derivative (Michael and Norton, Abstr., 1878, 407), which was regarded as the 3 : 5-compound. The corresponding di-iodo-derivative of *p*-aminobenzoic acid was also obtained by the latter authors. A study has now been made of these di-iodo-derivatives, and several other compounds have been prepared.

3-*Iodo*-p-*toluidine*, $NH_2 \cdot C_6H_3MeI$, m. p. 40°, obtained by the interaction of molecular proportions of iodine and *p*-toluidine, forms colourless needles; the *hydrochloride*, m. p. 188° (decomp.), and the *oxalate*, m. p. 119—120° (decomp.), are described. The *acetyl* derivative, m. p. 133°, crystallises in long, colourless prisms, and, when boiled with concentrated hydrochloric acid, yields 3 : 5-di-iodo-*p*-toluidine. The *benzoyl* derivative, m. p. 161°, forms long, colourless needles.

3-*Iodo*-p-*tolylcarbamide*, m. p. 187°, prepared by the action of potassium cyanate on 3-iodo-*p*-toluidine, forms thin, colourless plates. When 3-iodo-*p*-toluidine is heated with potassium thiobenzoate, benzenyl-4-amino-3-thiocresol (Hesse, Abstr., 1881, 597) is produced; its *platinichloride* crystallises with $1H_2O$.

3-*Iodo*-5(?)-*nitroaceto*-p-*toluidide*, $NO_2 \cdot C_6H_2MeI \cdot NHAc$, m. p. 202—203°, obtained by the action of nitric acid on 3-iodoaceto-*p*-toluidide, crystallises in prisms.

When *p*-toluidine (1 mol.) is warmed with iodine (2 mols.) in presence of water and calcium carbonate, 3 : 5-di-iodo-*p*-toluidine (Michael and Norton, *loc. cit.*) is produced; its *acetyl* derivative, m. p. 226°, forms stout, colourless prisms. 3 : 5-*Di-iodotoluene*, m. p. 44·5—45·5°, obtained by diazotising 3 : 5-di-iodo-*p*-toluidine in alcoholic solution and boiling the product, crystallises in yellow needles. 3 : 4 : 5-*Tri-iodotoluene*, m. p. 122—123°, prepared by the diazotisation of 3 : 5-di-iodo-*p*-toluidine dissolved in concentrated sulphuric acid, forms long, silky needles.

2-*Iodo*-3-*nitrotoluene*, $NO_2 \cdot C_6H_3MeI$, m. p. 67—68°, obtained by treating the product of the diazotisation of 3-nitro-*o*-toluidine with potassium iodide, crystallises in light yellow plates, and, on reduction with ferrous sulphate and ammonia, is converted into 2-*iodo*-m-*toluidine*, m. p. 41—42°, which forms long, flat prisms and yields an *acetyl* derivative, m. p. 135°. When the product of the diazotisation of 2-iodo-*m*-toluidine is treated with potassium iodide, 2 : 3-*di-iodotoluene*, m. p. 31—32°, is produced, which crystallises in colourless plates.

3-*Iodo*-4-*acetylaminobenzoic acid*, m. p. 230°, obtained by the oxidation of 3-iodoaceto-*p*-toluidide with potassium permanganate, forms long, colourless prisms. 2-*Iodo*-3-*acetylaminobenzoic acid*, m. p. 199°, prepared in a similar manner from 2-iodoaceto-*m*-toluidide, crystallises in prismatic needles. When 3-iodo-4-acetylaminobenzoic acid is boiled with concentrated hydrochloric acid, a mixture of *p*-aminobenzoic acid and 3 : 5-di-iodo-4-aminobenzoic acid is produced, the latter agreeing in properties with the compound obtained by Michael and Norton (*loc. cit.*) by the action of iodine monochloride on *p*-aminobenzoic acid. This compound can also be obtained, but only in poor yield, by the oxidation of 3 : 5-di-iodoaceto-*p*-toluidide with permanganate; its *ethyl* ester melts at 148°. 3-*Iodo*-4-*aminobenzoic acid*, m. p. 201—202°, is formed as an intermediate product in the preparation of 3 : 5-di-iodo-4-aminobenzoic acid by boiling 3-iodo-4-acetylaminobenzoic acid with hydrochloric acid, but is best prepared by the action of iodine monochloride on *p*-aminobenzoic acid. When potassium *p*-aminobenzoate is treated with iodine, *p*-iodoaniline is formed, but 3-iodo-4-aminobenzoic acid is not obtained. By the action of iodine on potassium 3 : 5-di-iodo-4-aminobenzoate, tri-iodoaniline, m. p. 184°, is produced.

3 : 4-*Di-iodobenzoic acid*, m. p. 257°, obtained by the action of potassium iodide on the product of the diazotisation of 3-iodo-4-aminobenzoic acid, crystallises in needles.

3 : 5-*Di-iodobenzoic acid*, m. p. 235°, prepared by the diazotisation of 3 : 5-di-iodo-4-aminobenzoic acid, forms pale yellow prisms.

3 : 4 : 5-*Tri-iodobenzoic acid*, m. p. 288°, obtained by adding potassium iodide to the product of the diazotisation of 3 : 5-di-iodo-4-aminobenzoic acid, crystallises in prismatic needles; its *sodium* salt crystallises with $2\frac{1}{2}H_2O$. 3 : 5-Di-iodo-4-hydroxybenzoic acid was also obtained from 3 : 5-di-iodo-4-aminobenzoic acid by means of the diazo-

reaction, but can be most conveniently prepared by the addition of iodine to a solution of *p*-hydroxybenzoic acid in potassium hydroxide. When dipotassium 3 : 5-di-iodo-4-hydroxybenzoate is heated with methyl iodide, *methyl* 3 : 5-*di-iodo*-p-*anisate*, m. p. 95°, is produced. 3 : 5-*Di-iodo*-p-*anisic acid*, m. p. 255—256° (decomp.), forms colourless prisms. E. G.

Halogen-amino-acids. VII. Iodine Derivatives of *o*-Toluidine. 3-Iodoaminobenzoic Acids. Henry L. Wheeler and Leonard M. Liddle (*Amer. Chem. J.*, 1909, 42, 498—505).—In an earlier paper (preceding abstract), it has been shown that by the action of iodine on *p*-toluidine, the 3-iodo- and 3 : 5-di-iodo-derivatives can be obtained.

A study has now been made of the action of iodine on *o*-toluidine, and it has been found that in this case only one derivative, namely, the 5-iodo-derivative (Artmann, Abstr., 1905, i, 879), is formed, and that this can be melted with iodine without further substitution being effected.

2 : 5-*Di-iodotoluene*, m. p. 30—31°, obtained by the action of potassium iodide on the product of the diazotisation of 5-iodo-*o*-toluidine, forms long, colourless plates; its *acetyl* derivative, m. p. 169°, and *benzoyl* derivative, m. p. 184°, crystallise in colourless needles. By the oxidation of the acetyl derivative with potassium permanganate, 5-*iodo*-2-*acetylaminobenzoic acid*, m. p. 235° (decomp.), is produced, which forms colourless needles, and, when warmed with hydrochloric acid, is converted into 5-iodo-2-aminobenzoic acid, m. p. 209—210°, which is identical with Grothe's β-iodoaminobenzoic acid (Abstr., 1879, 378). It follows from this that Grothe's α-iodo-amino- and α-iodonitro-benzoic acids are the 3-iodo-2-amino- and 3-iodo-2-nitro-derivatives and that his β-iodonitrobenzoic acid is the 5-iodo-2-nitro-compound. 3-*Iodo*-5-*nitrobenzoic acid*, m. p. 167°, prepared from 3-amino-5-nitrobenzoic acid (Hübner, Abstr., 1884, 315) by means of the diazo-reaction, forms long, slender, pale yellow needles; this compound is not identical with Grothe's γ-iodonitrobenzoic acid (*loc. cit.*), and the latter must therefore be the 3-iodo-4-nitro-derivative. 3-*Iodo*-5-*aminobenzoic acid*, m. p. 197°, obtained by reducing 3-iodo-5-nitrobenzoic acid with ferrous sulphate and ammonia, forms long, pale yellow crystals; its *hydrochloride* has been prepared. On adding potassium iodide to the product of the diazotisation of 3-iodo-5-aminobenzoic acid, 3 : 5-di-iodobenzoic acid is produced, identical with that obtained by the authors (*loc. cit.*) from 3 : 5-di-iodo-4-aminobenzoic acid. E. G.

Nitration of Diethylaniline. Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 297—303. Compare Abstr., 1900, i, 214).—A method of obtaining 3 : 4-dinitrodiethylaniline, 2 : 4-dinitrodiethylaniline, and 2 : 5-dinitrodiethylaniline from diethylaniline is described in detail.

3 : 4-*Dinitrodiethylaniline*, m. p. 95°, exists in a labile, yellow modification and a stable, orange form, also in an extremely labile, yellow form. It is converted by nitric acid (D 1·37) into 2 : 4 : 5-*trinitro-*

diethylaniline, m. p. 158°; if the nitric acid employed contains nitrous acid, then 2 : 4 : 5-*trinitroethylaniline*, m. p. 175°, is formed; the latter substance may also be prepared from the diethyl compound by treatment with sulphuric acid and sodium nitrite.

2 : 5-*Dinitrodiethylaniline* forms red crystals, m. p. 76°.

W. H. G.

Colour and Constitution. Alfred Werner (*Ber.*, 1909, 42, 4324—4328).—The author discusses the nature of the linking whereby highly coloured additive compounds are formed from polynitro-compounds and aromatic hydrocarbons or aromatic bases. The part played by the polynitro-compound in the formation of the additive-compound may be attributable to (*a*) hydrogen, either hydroxylic (in nitrophenols) or nuclear (in trinitrobenzene, picryl chloride, etc.), (*b*) the benzene nucleus, in virtue of its unsaturated character, (*c*) the nitro-group. The first alternative is improbable, since colourless trinitromesitylene forms coloured additive compounds. The second is negatived by the fact that chloropicrin and tetranitromethane form coloured compounds with aromatic hydrocarbons and amines. Since the formation of the labile additive compounds cannot be determined by the principal valencies of the nitro-group, the important conclusion is drawn that the appearance of the colour must be conditioned in some way by the supplementary valencies of the nitro-group.

With regard to the influence of the aromatic hydrocarbon in the production of the coloured additive compound, it is shown that tetranitromethane dissolves unsaturated aliphatic hydrocarbons and also unsaturated aliphatic acids (excepting those containing the double linking in the α-position to the carboxyl group) with a yellow colour, whilst the paraffin hydrocarbons, and also stearic acid, form colourless solutions. Consequently the formation of the additive compound is connected with the unsaturation of a hydrocarbon; as far as can be judged at present, the intensity of the colour of the additive compound increases with the unsaturation of the hydrocarbon.

The additive compounds of nitro-compounds and hydrocarbons, therefore, are molecular compounds, the formation of which depends on saturation of the supplementary valencies between nitro-groups and unsaturated carbon atoms.

From the fact that tetranitromethane develops an intense dark brown coloration with trimethylamine, the author draws the conclusion that in the additive compounds of polynitro-compounds and amines the nitro-group is joined, not to unsaturated carbon atoms, but to the tervalent nitrogen. C. S.

Electrolytic Reduction of 2-Nitrotoluene-4-sulphonyl Chloride. Fritz Fichter and Walter Bernoulli (*Ber.*, 1909, 42, 4308—4311).—Aromatic sulphonyl chlorides containing a nitro-group are reduced much more smoothly than the compounds described previously (Abstr., 1907, i, 690), because the nitro-group is first reduced to an amino-group, and the resulting basic substance readily

dissolves in the cathodic acid liquor. Thus a suspension of 2-nitrotoluene-4-sulphonyl chloride in alcoholic sulphuric acid is readily reduced at a lead cathode below 20°, using a current density of 0·07 amperes per sq. cm., and one and a-half times the quantity of electricity theoretically required. The product is 2-*aminotolyl* 4-*mercaptan sulphate*, which readily changes to the *sulphate* of 2-aminotolyl 4-disulphide by keeping in a loosely closed vessel. 2-*Aminotolyl* 4-*disulphide*, m. p. 82°, forms almost colourless needles, and yields an *acetyl* derivative, m. p. 239°. C. S.

Nitration. VI. Nitroaniline Derivatives of Organic Acids. J. Bishop Tingle and C. E. Burke (*J. Amer. Chem. Soc.*, 1909, 31, 1312—1319).—By the nitration of various *N*-acylanilides, Tingle and Blanck (Abstr., 1908, i, 778, 893) have prepared a large number of substances, the constitutions of some of which were not ascertained at the time, since their determination offered considerable difficulty. The present work was undertaken for the purpose of elucidating the structure of these compounds. Two series of experiments have been carried out; in the first series, *o*-, *m*-, and *p*-nitroanilines were treated at the ordinary temperature with various organic acids in presence of a solvent, whilst in the second series the mixture of acid and nitroaniline was fused, and the heating continued until the reaction was complete. The acids employed were formic, acetic, stearic, oxalic, succinic, tartaric, citric, benzoic, salicylic, phthalic, and picric acids. The nitration products of propionanilide were also investigated.

The product obtained by the nitration of propionanilide with nitric acid or a mixture of nitric and acetic acids has proved to be unchanged propionanilide, whilst the substance obtained by the action of a mixture of nitric and sulphuric acids is p-*nitropropionanilide*, m. p. 182°, which forms yellowish-brown plates.

Stearic acid does not unite with any of the nitroanilines; the products obtained by Tingle and Blanck in their attempts to nitrate stearanilide consisted of impure stearanilide.

Oxalic acid does not combine with the nitroanilines. The substances obtained by the action of nitric acid on oxalanilide prove to be impure oxalanilide. The yellow substance, prepared by the action of a mixture of nitric and oxalic acids on oxalanilide, was p-*nitro-oxalanilide*, m. p. 265°.

Succinic acid does not react with *o*- or *p*-nitroanilines, but on adding the acid to melted *m*-nitroaniline, m-*nitrosuccinylphenylimide*,

$$\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}\!\!>\!N\cdot C_6H_4\cdot NO_2,$$

m. p. 172°, is obtained, which forms pale yellow crystals. The compound obtained by Tingle and Blanck on nitrating succinanil was the unchanged anil, whilst the compound prepared by the action of a mixture of nitric and oxalic acids on succinanilide was a *dinitro*-derivative, m. p. 240—243°.

Tartaric acid does not yield a compound with *o*-nitroaniline, but with *m*-nitroaniline it gives m-*nitroaniline* m-*nitrophenyltartramate*,

$NO_2 \cdot C_6H_4 \cdot NH_2$, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CO_2H$, m. p. 172°, in the form of small, yellow crystals, and with *p*-nitroaniline it gives p-*nitrophenyltartramic acid*,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CO_2H,$$

m. p. 218°, which forms bright yellow crystals. The compound obtained by Tingle and Blanck from tartranilide and a mixture of nitric and oxalic acids is found to be s-m-*dinitrotartranilide*,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CO \cdot NH \cdot C_6H_4 \cdot NO_2,$$

m. p. 224°.

Citric acid does not give derivatives with *o*- and *p*-nitroanilines, but with the *m*-compound yields a *di*-m-*nitroaniline citrate*, m. p. 207°. The compound obtained by Tingle and Blanck by the action of a mixture of nitric and oxalic acids on citranilide is *citryl tris*-m-*nitroanilide*, $C_3H_5O(CO \cdot NH \cdot C_6H_4 \cdot NO_2)_3$, m. p. 122°. The other products obtained by the action of nitric acid on citranilide consisted of the impure anilide.

Salicylic and phthalic acids do not react with any of the nitroanilines. Benzoic acid yields small quantities of compounds when fused with *o*- and *m*-nitroaniline, but these have not been identified.

Picric acid does not react with *o*-nitroaniline, but yields the picrates of the meta- and para-isomerides, which have m. p. 147° and 100° respectively. The compound obtained by Tingle and Blanck by the action of a mixture of nitric and oxalic acids on picranilide is a *tetranitrodiphenylamine*, $NO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_2(NO_2)_3$, m. p. 197—200°; by the action of nitric acid on diphenylamine, another *tetranitrodiphenylamine*, m. p. 275°, is produced. E. G.

d-**Leucyl**-*l*-**tryptophan.** Hans Fischer (*Ber.*, 1909, **42**, 4320—4322).—Formyl-*l*-leucine is converted by Fischer's method (Abstr., 1906, i, 808) into *l*-bromo*iso*hexoic acid, and this by phosphorus pentachloride into *l*-bromo*iso*hexoyl chloride, which is condensed with tryptophan (Abderhalden and Kempe, Abstr., 1907, i, 652) to form l-*bromo*iso*hexoyltryptophan*. This oily product is dissolved in 25% ammonium hydroxide, whereby d-*leucyl*-l-*tryptophan*,

$$C_8H_6N \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CH(NH_2) \cdot C_4H_9,$$

is obtained in needles. The dipeptide does not show the biuret reaction, has a sweet taste, is precipitated from acid solutions by phosphotungstic acid, and has $[\alpha]_D^{20}$ −68·97° in *N*-hydrochloric acid. It melts at 189° (corr.), but immediately crystallises to a substance, probably a tautomeride, melting at 225—230°, which can also be produced by crystallising the dipeptide from water, alcohol, and ether. Prepared by the latter method, the *substance*, $C_{17}H_{23}O_3N_3$, darkens at 230°, and has m. p. 243°; in *N*-hydrochloric acid it has $[\alpha]_D^{20}$ −73·27°. C. S.

Maleic and Fumaric Derivatives of *p*-Aminophenols. Arnaldo Piutti (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 312—326).—The theoretical part of this paper has been already published (Abstr., 1908, i, 783), the author now giving the following experimental results.

p-*Hydroxyphenylmaleinamic acid*, $OH\cdot C_6H_4\cdot N{:}C(OH)\cdot CH{:}CH\cdot CO_2H$, prepared from *p*-aminophenol and maleic anhydride, separates in crusts of slender, yellow needles or in greenish-yellow prisms, m. p. 182°, and gives no coloration with ferric chloride.

p-*Methoxyphenylmaleinamic acid*, $OMe\cdot C_6H_4\cdot N{:}C(OH)\cdot CH{:}CH\cdot CO_2H$, prepared from *p*-anisidine and maleic anhydride, crystallises in canary-yellow, dichroic needles or in yellow prisms exhibiting slight greenish-yellow pleochroism, m. p. 180—181°, and with ferric chloride gives a yellowish-brown coloration changing to violet.

p-*Ethoxyphenylmaleinamic acid*, $OEt\cdot C_6H_4\cdot N{:}C(OH)\cdot CH{:}CH\cdot CO_2H$, prepared from *p*-phenetidine and maleic anhydride, crystallises in spherical aggregates of slender, yellow needles or in tufts of canary-yellow prisms, showing slight pleochroism, m. p. 181—182° (impure), and with ferric chloride gives a yellowish-brown coloration changing to intense violet.

p-*Hydroxyphenylmaleimide*, $\begin{matrix}CH\cdot C(:N\cdot C_6H_4\cdot OH)\\ \|\qquad\qquad\quad\\ CH\text{——————}CO\end{matrix}\!\!>O$, obtained by heating *p*-hydroxyphenylmaleinamic acid with acetyl chloride in acetone solution, separates in tufts or rosettes of acicular crystals, m. p. 154—155°.

p-*Methoxyphenylmaleimide*, $C_{11}H_9O_3N$, forms colourless, tubular crystals or small needles, m. p. 145—146°.

p-*Ethoxyphenylmaleimide*, $C_{12}H_{11}O_3N$, forms colourless, tubular crystals or silky needles, m. p. 127°, gives the normal molecular weight in freezing acetic acid, and, on reduction with sodium amalgam, yields *p*-ethoxyphenylsuccinamic acid and its imide (compare Abstr., 1896, i, 223). With aqueous or alcoholic sodium hydroxide it yields *p*-ethoxyphenylmaleinamic acid, whilst concentrated hydrochloric acid resolves it into *p*-aminophenol and fumaric acid. When treated with sodium ethoxide it gives the reddish-violet *compound*, $C_{14}H_{16}O_4NNa$, which, with sulphuric acid, yields the *compound*, $C_{14}H_{17}O_4N$, as a reddish-brown powder.

s-p-*Methoxyphenylmaleimide*, $\begin{matrix}CH\cdot CO\\ \|\\ CH\cdot CO\end{matrix}\!\!>N\cdot C_6H_4\cdot OMe$, prepared by the action of phosphoric oxide on *p*-methoxyphenylmaleinamic acid, forms slender, yellow needles, m. p. 148·5°, and exhibits normal cryoscopic behaviour in acetic acid.

s-p-*Ethoxyphenylmaleimide*, $C_{12}H_{11}O_3N$, obtained from the corresponding amic acid by sublimation or by the action of phosphoric oxide, forms yellow needles, m. p. 134—135°, and has the normal molecular weight in freezing acetic acid.

p-*Hydroxyphenylfumaric diamide*,

$$OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH{:}CH\cdot CO\cdot NH\cdot C_6H_4\cdot OH,$$

exists in two modifications: (1) white, decomp. at 220°, obtained by heating the acid fumarate of *p*-aminophenol at 200° in a current of carbon dioxide, and (2) yellow, which is obtained by crystallising the white variety from acetic acid, and is identical in properties with the white form.

p-*Methoxyphenylfumaric diamide*, $C_{18}H_{18}O_4N_2$, forms thin, white,

silky plates, m. p. 216°, and a yellow, apparently amorphous powder, having corresponding properties.

p-*Ethoxyphenylfumaric diamide*, $C_{20}H_{22}O_4N_2$, forms microscopic, colourless needles, m. p. 223°, and yellow, irregular plates, exhibiting marked pleochroism. T. H. P.

$\Delta^{1:5}$-Dihydrophenol or Δ^{2}-*cyclo*Hexenone. Arthur Kötz and Th. Grethe (*J. pr. chem.*, 1909, [ii], 80, 473—510).—$\Delta^{1:5}$-*cyclo*-Hexadienol cannot be prepared from aliphatic compounds, but is obtained from *cyclo*hexanone in several ways.

2-*Chloro*(or *bromo*)cyclo*hexanone* is obtained by passing chlorine (or carbon dioxide charged with bromine vapour) into a mixture of *cyclo*hexanone, calcium carbonate, and water at 25—30°; the chloro-derivative has m. p. 23°, b. p. 82°/13 mm., and the bromo-derivative has b. p. 89°/14 mm. $\Delta^{1:5}$-*cyclo*Hexadienol is obtained from these compounds directly by heating with sodium acetate and glacial acetic acid or with ethereal aniline (best method), or indirectly by hydrolysing them by concentrated aqueous potassium hydroxide, the resulting cyclo*hexanon*-2-*ol*, m. p. 92—92·5°, being converted into the dihydrophenol by anhydrous oxalic acid at 100—110°, or by Tschugaeff's xanthogenic reaction.

$\Delta^{1:5}$-cyclo*Hexadienol*, b. p. 63°/14 mm., D^{18} 0·9868, n 1·4796, forms a *semicarbazone*, $C_7H_{11}ON_3$, m. p. 161°, and with 1 mol. of hydroxylamine hydrochloride an *oxime*, C_6H_9ON, m. p. 75—76°, which yields aniline by heating with acetic anhydride and then with sodium hydroxide. When the dihydrophenol is kept for eight days in a methyl-alcoholic solution of hydroxylamine (2 mols.), 3-*hydroxyamino*cyclo*hexanoneoxime*,

$$OH\cdot NH\cdot CH\begin{matrix}<CH_2\cdot C(:NOH)\\ CH_2\text{———}CH_2\end{matrix}>CH_2,$$

m. p. 49—51°, is obtained, which dissolves in acids and in alkalis, reduces warm Fehling's solution, and is oxidised by mercuric oxide in boiling water to cyclo*hexane*-1 : 3-*dioxime*, m. p. 155·5°, which yields cyclo*hexane*-1 : 3-*dione*, m. p. 105—106°, by hydrolysis by 10% sulphuric acid. 3-Hydroxylamino*cyclo*hexanoneoxime is reduced by sodium and boiling alcohol to 1 : 3-*diamino*cyclo*hexane*, the *platinichloride* of which, $C_6H_{10}(NH_2)_2,H_2PtCl_6$, has m. p. 256° (decomp.).

3-*Chloro*cyclo*hexanone*, b. p. 91—92°/14 mm., is obtained by passing dry hydrogen chloride into a dry ethereal solution of $\Delta^{1:5}$-*cyclo*-hexadienol. The dihydrophenol absorbs bromine, forming a dibromo-additive compound, which yields phenol by loss of 2 mols. of hydrogen bromide. The dihydrophenol also yields a *benzylidene* compound, $CHPh{:}C\begin{matrix}<CH_2\cdot CH_2\\ CO\text{—}CH\end{matrix}>CH$, b. p. 172—175°/15 mm., by treatment with benzaldehyde and cold alcoholic sodium ethoxide.

The action of carbon dioxide on an ethereal solution of $\Delta^{1:5}$-*cyclo*-hexadienol in the presence of sodium leads to the formation of Δ^{3}-cyclo*hexene*-2-*one*-1-*carboxylic acid* ($\Delta^{1:3}$-*dihydrosalicylic acid*), the *ethyl* ester of which, prepared from the silver salt, has b. p. 115—117°/15 mm. The constitution of the acid is proved as follows.

In the presence of sodium ethoxide, $\Delta^{1:5}$-*cyclo*hexadienol condenses with ethyl oxalate to form the *ethyl* ester,

$$CO_2Et\cdot CO\cdot CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CH_2\cdot CH_2\\CO\text{—}CH\end{matrix}\begin{matrix}>\\>\end{matrix}CH,$$

which gives a red coloration with ferric chloride, and loses carbonic oxide by distillation in a vacuum, yielding ethyl $\Delta^{1:3}$-dihydrosalicylate, b. p. 115°/14 mm. (blue colour with ferric chloride), identical with the preceding ester. Since by treatment with potassium and methyl iodide in xylene the ester yields the *methyl* homologue,

$$CO_2Et\cdot CMe\begin{matrix}<\\>\end{matrix}\begin{matrix}CH_2\cdot CH_2\\CO\text{—}CH\end{matrix}\begin{matrix}>\\>\end{matrix}CH,$$

b. p. 110—125°/12 mm., which can be converted into 2-methyl*cyclo*hexanone, it must have the constitution assigned to it, and not that of Δ^6-cyclo*hexen*-2-*one*-1-*carboxylic acid*, m. p. 128°, which could not form a methyl derivative under the preceding conditions. This acid is obtained by heating ethyl 1-bromo*cyclo*hexan-2-one-1-carboxylate with sodium acetate and acetic acid, or the corresponding bromo-compound with ethereal aniline, and hydrolysing the *ethyl* Δ^6-cyclo*hexen*-2-*one*-1-*carboxylate*, b. p. 103°/12 mm., produced. It yields $\Delta^{1:5}$-*cyclo*hexadienol by distillation with soda-lime.

When an ethereal solution of *cyclo*hexanone is gently boiled with sodamide and the resulting sodium derivative treated with carbon dioxide, cyclo*hexan*-2-*one*-1-*carboxylic acid* is obtained ultimately; the *barium* and *silver* salts are mentioned, and the *ethyl* ester has b. p. 108—109°/12 mm.

Ethyl 4-methyl*cyclo*hexan-2-one-1-carboxylate yields ethyl 1-bromo-4-methyl*cyclo*hexan-2-one-1-carboxylate by bromination, which is boiled with ethereal aniline, whereby *ethyl* 4-*methyl*-Δ^6-cyclo*hexen*-2-*one*-1-*carboxylate*, b. p. 113°/12 mm., is produced; the corresponding *acid* has m. p. 153°, and by distillation with soda-lime yields 5-*methyl*-Δ^2-cyclo*hexenone*, b. p. 189°, which forms a *semicarbazone*, m. p. 158°.

C. S.

Synthesis of Octa-, Deca-, and Dodeca-methylene Compounds of the Aliphatic Series. Julius von Braun [and A. Trümpler] (*Ber.*, 1909, 43, 4541—4554).—On coupling two molecules of phenyl δ-iodobutyl ether by means of sodium, *aθ*-diphenoxyoctane is obtained in good yield, and the yield is increased when the same process is applied to the phenyl ethers of iodoamyl or iodohexyl to form diphenoxy-decane and -dodecane derivatives. The further the iodine is distant from the phenoxy-group the more the compound tends to behave as a simple non-substituted alkyl iodide.

The replacement of the phenoxy-group by iodine, effected by heating with hydriodic acid in sealed tubes, becomes more difficult the larger the distance between the phenoxy-groups. Whereas diphenoxypentane only requires heating at 120° with 2 c.c. of fuming hydriodic acid per gram of ether, both diphenoxyhexane and diphenoxyoctane require heating at 130—135° with 3 c.c. of the acid; diphenoxydecane must be heated at 150° with 4 c.c. of the halogen acid, and to convert diphenoxydodecane, it is necessary to heat with a large excess of

hydriodic acid at 175—180°. This method of preparing di-iodo-paraffins is not available much higher in the series.

Phenyl δ-iodobutyl ether is condensed in presence of sodium to *aθ*-diphenoxyoctane, $OPh\cdot[CH_2]_8\cdot OPh$ (compare Solonina, Abstr., 1899, i, 681), m. p. 80°, which, when heated with hydrogen iodide at 135°, forms *aθ-di-iodo-octane*, $I\cdot[CH_2]_8\cdot I$, b. p. 179—180°/13 mm.

aθ-Diphenylthioloctane, $C_8H_{16}(SPh)_2$, prepared by the interaction of di-iodo-octane, sodium, and thiophenol, is a colourless, crystalline solid, m. p. 83°.

aθ-Dianilino-octane, $C_6H_{16}(NHPh)_2$, is formed quantitatively by the interaction of the iodide with aniline. It has m. p. 61—62°; the *picrate* and *nitroso*-derivative are oily; the *benzoyl* derivative has m. p. 110—112°.

The condensation of phenyl ε-iodoamyl ether by sodium gives rise to compounds which may be separated by steam distillation into a volatile and a non-volatile product. The former, b. p. 117—120°/15 mm., consists of a mixture of phenyl-*n*-amyl ether and phenylamylenyl ether, $CH_2{:}CH\cdot[CH_2]_3\cdot OPh$; when the mixture is heated with hydrogen iodide, *n*-amyl iodide, b. p. 62°/20 mm., and 1 : 4-di-iodopentane, b. p. 140°/20 mm., are obtained, the structure of the latter being proved by condensation with aniline to be phenyl-2-methylpyrrolidine (Scholtz and Friemehlt, Abstr., 1899, i, 541), b. p. 136—138°/16 mm.; picrate, m. p. 108—109°; platinichloride, m. p. 135°.

Amyl iodide, on prolonged heating with potassium cyanide, forms *hexonitrile*, a colourless liquid of penetrating, but not unpleasant, odour, b. p. 160°.

The non-volatile portion, *aκ-diphenoxydecane*, has m. p. 85°; it yields *aκ-di-iododecane*, $C_{10}H_{20}I_2$, a faintly-coloured oil, b. p. 212—215°/16 mm., which crystallises in very stable, lustrous, glass-like crystals, m. p. 29—30°. The corresponding *aκ-diphenylthioldecane* has m. p. 85°.

Decane-*aκ*-dicarboxylic acid, m. p. 125°, is identical with an acid described by Nördlinger (Abstr., 1890, 1237). The *nitrile*, prepared by heating di-iododecane with potassium cyanide, is a colourless, almost odourless liquid, m. p. 225—228°/17 mm., which solidifies when cooled with ice.

Di-iododecane, when heated with potassium phthalimide at 180—190°, forms a *phthalimide*,

$$C_6H_4\begin{<}CO\\CO\end{>}N\cdot[CH_2]_{10}\cdot N\begin{<}CO\\CO\end{>}C_6H_4,$$

m. p. 136°. The corresponding *phthalamic acid*,

$$C_{10}H_{20}(NH\cdot CO\cdot C_6H_4\cdot CO_2H)_2,$$

separates in well-formed, colourless crystals, m. p. 129°. When the phthalimide is heated for four hours at 180° with hydrogen chloride, *aκ*-diaminodecane, m. p. 60°, is formed. The dibenzoyl derivative has m. p. 152°.

Phenyliodohexyl ether is condensed by sodium to volatile products and *aμ-diphenoxydodecane*. It is converted with difficulty into *aμ*-di-iododecane, m. p. 41°.

When decane-*aκ*-dicarboxylnitrile is reduced, the *hydrochloride* of *aμ-diaminododecamethane* is formed; this does not melt at 250°; the

platinichloride, decomp. 225°. The free diamine is a colourless solid, m. p. 66—67°; the *benzoyl* derivative has m. p. 153°, and the benzenesulphonyl compound crystallises in nacreous plates, m. p. 99°.

E. F. A.

Monohalogenated Phenols. William J. Wohlleben (*Ber.*, 1909, **42**, 4369—4375).—Commercial *o*-chlorophenol contains phenol, as it yields phenyl benzoate, m. p. 70°, on benzoylation. To purify it, it is conveniently shaken with an excess of potassium carbonate and the phenol present extracted with ether. o-*Chlorophenyl acetate* is a clear, colourless oil, b. p. 103°/15 mm., m. p. −20·5° to −19·5°, D_4^{20} 1·2166. o'-*Chlorophenyl* m-*nitrobenzoate* crystallises in characteristic bunches of prisms, m. p. 98°.

m-*Chlorophenyl acetate* is an oil, b. p. 116·5°/21 mm., D_4^{20} 1·2209; it crystallises in needles, m. p. −1·5° to 0·5°; the *benzoate* crystallises in glistening prisms, m. p. 71—72°; the m-*nitrobenzoate* separates in colourless, matted needles, m. p. 94—95°. *m*-Chlorophenetole (compare Guttermann, *Annalen*, 1907, **357**, 349) is a clear oil with a pleasant odour; b. p. 204—205°/717 mm., D_4^{20} 1·1712. o-*Chloro*-p-*hydroxyazobenzene*, $NPh{:}N{\cdot}C_6H_3Cl{\cdot}OH$, crystallises in glistening, orange-red needles, m. p. 114—115°.

p-*Chlorophenyl acetate* is an oil, b. p. 108°/12·5 mm., D_4^{20} 1·2248; it forms long, crystal needles, m. p. 7—8°. All three chlorophenols dissolve when shaken with concentrated sodium carbonate, and are precipitated by carbon dioxide. p'-*Chlorophenol* m-*nitrobenzoate* forms lustrous, silky, concentrically grouped needles, m. p. 124·5°.

o-*Bromophenyl acetate* is a clear oil with an ethereal odour, b. p. 149—150°, D_4^{20} 1·4924.

m-*Bromophenyl acetate* has b. p. 149°/40 mm., D_4^{20} 1·5478. It does not mix with benzene; the *benzoate* crystallises in colourless, microscopic prisms or rhombic plates, m. p. 86°.

p-*Bromophenyl acetate* is an oil of unpleasant odour, b. p. 128°/35 mm., which forms colourless needles, m. p. 21·5°; the benzoate, which has been variously described, crystallises from alcohol in colourless, rhombic plates, m. p. 104°.

p-*Iodophenyl acetate* forms colourless plates, m. p. 32—32·5°; the *benzoate* crystallises in colourless, six-sided or rhombic plates, or in matted needles, m. p. 118·5°—119·5°; the m-*nitrobenzoate* separates in lustrous, long, colourless needles, m. p. 120—121°; the *benzenesulphonate* crystallises in long, colourless plates, or in bunches of lustrous, matted needles, m. p. 52—53°.

E. F. A.

Preparation of Aromatic Nitrohydroxy-compounds. Richard Wolffenstein and Oskar Boeters (D.R.-P. 214045. Compare Abstr., 1908, i, 629).—It has been shown previously that the action of nitric acid on aromatic hydrocarbons in the presence of mercury results in the formation of nitrohydroxylated products; it is now found that nitrous acid or the oxides of nitrogen react in a similar manner. The treatment of benzene with nitrogen peroxide in the presence of mercury yields 2 : 4-dinitrophenol, whilst with fuming nitric acid at a high temperature picric acid is obtained.

F. M. G. M.

Preparation of Arylalkyl-*p*-aminophenols. Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 213592. Compare Abstr., 1909, i, 914).—The following compounds prepared by the reduction (with zinc in alkaline solution) of the condensation products from substituted *p*-aminophenols and aromatic aldehydes are employed for photographic purposes.

3-*Chloro*-4-*benzylideneaminophenol*, m. p. 180—181°, from the condensation of benzaldehyde with 3-chloro-4-aminophenyl sulphate, yields, on reduction, 3-*chloro*-4-*benzylaminophenol*, which was not obtained in crystalline form; its crystalline *hydrochloride* has m. p. 195° (decomp.).

4-*Benzylideneamino*-m-*cresol*, m. p. 133°, prepared from 4-amino-*m*-tolyl sulphate and benzaldehyde, yields, by reduction, 4-*benzylamino*-m-*cresol*, which separates in the form of its sparingly soluble *sodium* salt; the *hydrochloride* has m. p. 220° (decomp.), and from this, on treatment with sodium sulphide, the free base, m. p. 84°, is obtained.

F. M. G. M.

Estimation of Ortho- and Para-Sulpho-groups in Phenolsulphonic Acids. Julius Obermiller (*Ber.*, 1909, 42, 4361—4369).—It is well known that by treatment with bromine, phenolsulphonic acids lose their *o*- and *p*-sulphonic groups, which are eliminated as sulphuric acid. The latter can be estimated gravimetrically, but to avoid too high results the following directions must be closely followed.

The bromine solution consists of water containing 1 per cent. of sodium bromate (or 1·1% of potassium bromate) and 5% of potassium bromide; it contains 3·1—3·2% of potential bromine. The phenolsulphonate, 0·2 to 0·3 gram, with three times the weight of barium chloride, and 10 c.c. of hydrochloric acid, D 1·19, are diluted to 100 c.c. with water. The solution is heated to 60—65°, and slowly treated, with certain precautions, with the bromine solution until a faint persistent, yellow colour is produced. A little alcoholic phenol is added to absorb the excess of bromine, and then sufficient alcohol to dissolve the tribromophenol. The liquid is boiled and decanted while warm from the barium sulphate, which is repeatedly washed in the beaker with 50% alcohol and then with hot water. The barium sulphate is finely filtered and weighed in the usual way. Barium *o*-phenolsulphonate, magnesium *p*-phenolsulphonate, and barium phenol-2 : 4-disulphonate (Abstr., 1907, i, 910) have been satisfactorily treated by this process, although the results are still a little high. Sulpho-groups in the para-position are eliminated with greater difficulty than those in the ortho-position. Of the salts of doubtful constitution, previously obtained by the fractional crystallisation of the salts prepared from the sulphonation products of phenol (*loc. cit.*), the "aluminium salt of the para-acid" proves to be the magnesium salt, the "magnesium salt of the ortho-acid" to be the magnesium salt of the para-acid, the "barium salt of the ortho-acid" to be barium chloride, and the "magnesium salt of the disulphonic acid" to be a mixture of calcium phenol-2 : 4-disulphonate and magnesium *o*-phenolsulphonate.

C. S.

Abnormal Reduction of an Aromatic Nitro-compound with Tin and Hydrochloric Acid and an Interesting Case of Dimorphism. Otto de Vries (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 305—306; *Rec. trav. chim.*, 1909, 28, 395—407).—3-Nitro-4-methoxytoluene, when reduced with iron and acetic acid, yields the corresponding amine, whilst treatment with tin and hydrochloric acid leads to the formation of 6-*chloro*-3-*amino*-p-*tolyl methyl ether*, which forms colourless needles, m. p. 106° (corr.); the *acetyl* derivative has m. p. 115° (corr.). In order to arrive at the constitution of the compound, it was converted into 3 : 6-*dichloro*-p-*tolyl methyl ether*, which was obtained in a labile modification, crystallising in needles, m. p. 29°, and a stable modification, forming flat crystals, m. p. 44°. The fused substance, when cooled, yields the labile variety, which, by inoculation or in an infected region, passes spontaneously into the stable form.

W. H. G.

2 : 5-Diphenylphenol. Fritz Fichter and Otto Walter (*Ber.*, 1909, 42, 4311—4315).—2 : 5-Diphenylphenol (Abstr., 1903, i, 481) yields 2 : 5-*diphenylphenyl* p-*toluenesulphonate*, $C_{25}H_{20}O_3S$, m. p. 102°, by boiling with alcoholic potassium hydroxide, and *p*-toluenesulphonyl chloride. p-*Nitrobenzeneazodiphenylphenol*, $OH\cdot C_6H_2Ph_2\cdot N_2\cdot C_6H_4\cdot NO_2$, red needles, decomposing at 243—245°, is obtained by the action of diazotised *p*-nitroaniline on alcoholic diphenylphenol in alkaline solution.

The attempt to produce a benzene ring by the condensation of styrylitaconic acid (Abstr., 1901, i, 594) by acetic anhydride at 130° resulted in the formation of the *anhydride*,

$$\begin{matrix} O\text{—}CO \\ | \\ CO\cdot CH_2 \end{matrix}\!\!>\!C\!:\!CH\cdot CH\!:\!CHPh,$$

m. p. 180°.

The nitration of phenylsuccinic acid by nitric acid, D 1·52, at 0° results in the formation of *o-nitrophenylsuccinic acid*, m. p. 188°, and p-*nitrophenylsuccinic acid*, m. p. 218°—220° (decomp.); p-*acetylamino-phenylsuccinic acid* has m. p. 218°.

The reduction of *o*-nitrophenylsuccinic acid by ammoniacal ferrous sulphate yields *dihydrocarbostyril-γ-carboxylic acid*,

$$C_6H_4\!<\!\begin{matrix} CH(CO_2H)\cdot CH_2 \\ | \\ NH\text{—————}CO \end{matrix},$$

m. p. 223°, which separates from water in colourless needles. C. S.

The Fluorene Series. I. Julius Schmidt and Hermann Stützel (*Annalen*, 1909, 370, 1—40. Compare Abstr., 1908, i, 415; Schmidt and Mezger, Abstr., 1907, i, 43; Schmidt and Söll, *ibid.*, 1054).—Although fluorenoneoxime is converted by zinc and acetic acid into 9-aminofluorene, when it is reduced by tin and hot concentrated hydrochloric acid it yields fluorenyl ether, the formation of which may be explained thus: $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C\!:\!NOH \longrightarrow \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CO \longrightarrow \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH\cdot OH \longrightarrow \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH\cdot O\cdot CH\!<\!\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$. The most remarkable property of this substance is its red colour, which cannot be due to a

quinonoid structure, for fluorene and 9-hydroxyfluorene are quite colourless, but is probably the result of an accumulation of benzene nuclei.

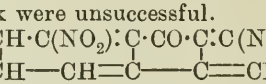
It is shown that the known 9-hydroxyfluorene is directly connected with α-9-aminofluorene, since it yields α-9-acetoxyfluorene when heated with acetic anhydride; attempts to prepare the 9-hydroxyfluorene, corresponding with β-9-aminofluorene, were unsuccessful.

When 9-acetylaminofluorene is warmed with nitric acid, it yields 1 : 8-dinitrofluorenone, many derivatives of which have been prepared. The behaviour of 1 : 8-dinitrofluorenone towards stannous chloride and hydrochloric acid is remarkable, in that a nitro-group is eliminated with the formation of 1-amino-9-hydroxyfluorene, a compound not without interest, for it is red, and the substances derived from it are also intensely coloured. When 1 : 8-dinitrofluorenoneoxime is reduced with tin and hydrochloric acid, it likewise yields 1-amino-9-hydroxyfluorene, but when treated with zinc dust and acetic acid it is converted into 1 : 9-diaminofluorene.

Fluorenyl ether crystallises in red prisms, m. p. 254—255°, and when warmed with concentrated nitric acid yields a yellow *substance*, m. p. about 285°.

α-9-Hydroxyfluorene, m. p. 153°, is obtained by the action of nitrous acid on either α- or β-9-aminofluorene, possibly because β-9-hydroxyfluorene is labile and passes into the stable α-form; the *benzoate*, $C_{20}H_{14}O_2$, crystallises in colourless leaflets, m. p. 161°.

When 9-aminofluorene is reduced with amyl alcohol and sodium, it yields an oily *substance*, which is either 9-aminodihydrofluorene or 9-aminotetrahydrofluorene; the *picrolonate* forms yellow crystals, m. p. 218°; attempts to reduce 9-aminofluorene with hydrogen in the presence of platinum-black were unsuccessful.

1 : 8-*Dinitrofluorenone*,  , crystallises in glistening, yellow prisms, m. p. 196—197°, and is oxidised by potassium permanganate, yielding *o*-nitrobenzoic acid; the *phenylhydrazone*, $C_{19}H_{12}O_4N_4$, forms scarlet needles, m. p. 206—207°; the *semicarbazone*, $C_{14}H_9O_5N_5$, is a brownish-yellow powder, which does not melt at 300°.

1 : 8-*Dinitrofluorenoneoxime*, $C_{13}H_7O_5N_3$, crystallises in pale yellow nodules, m. p. 250°; the *benzoyl* derivative, $C_{20}H_{11}O_6N_3$, forms pale yellow needles, m. p. 218—220°; the *acetyl* derivative, $C_{15}H_9O_6N_3$, crystallises in brownish-yellow needles, m. p. 178°; the *methyl ether*, $C_{14}H_9O_5N_3$, forms small, pale yellow, crystalline nodules, m. p. about 150° (decomp.).

1-*Amino*-9-*hydroxyfluorene*, $C_{13}H_{11}ON$, crystallises in dark red needles, m. p. 142°; the *acetyl* derivative, $C_{15}H_{13}O_2N$, forms small, brownish-yellow crystals, m. p. 200°; the *benzoyl* derivative,

$$C_{20}H_{15}O_2N,$$

crystallises in flesh-coloured needles, m. p. 260°; the position of the acyl group in the compounds just described is not known; the *hydrochloride*, $C_{13}H_{11}ON,HCl$, forms small, brownish-yellow crystals, m. p. 290° (decomp.); the *nitrate* forms small, brown crystals, and

does not melt at 300°; the *picrolonate*, $C_{23}H_{19}O_6N_5$, forms greenish-yellow crystals, m. p. 246° (decomp.); the *additive* product with phenylcarbimide, $C_{27}H_{21}O_3N_3$, forms small, red crystals, m. p. 262°. The *diazo*-derivatives couples with phenols and amines, yielding *azo*-dyes, and when boiled with water yield 1 : 9-*dihydroxyfluorene*, a reddish-brown, crystalline substance, m. p. 218—220°; the *diacetate* crystallises in reddish-brown needles, and does not melt at 300°.

1 : 9-*Diaminofluorene*, $C_{13}H_{12}N_2$, forms small, white crystals, m. p. about 120°; the *diacetyl* derivative, $C_{17}H_{16}O_2N_2$, crystallises in white leaflets, m. p. 293°; the *dibenzoyl* derivative, $C_{27}H_{20}O_2N_2$, forms small, white needles, m. p. about 310°; the *picrate* crystallises in greenish-yellow leaflets, m. p. 205° (decomp.); the *picrolonate*,

$$C_{23}H_{20}O_5N_6,$$

forms yellowish-brown crystals, and decomposes at about 235°; 1 : 9-*diphenylcarbamidofluorene*, prepared from the diamine and phenylcarbimide, forms small, white crystals, m. p. 258—260°.

W. H. G.

Cholesterol. I. The Xanthogen Reaction. Leo Tschugaeff and A. Gasteff (*Ber.*, 1909, **42**, 4631—4634).—The authors have applied the xanthogen reaction (Abstr., 1900, i, 129; 1905, i, 71) to cholesterol. In order to avoid molecular rearrangement in the formation of potassium cholesteroxide, the compound was prepared by the action of a toluene solution of cholesterol on potassium amyloxide.

Methyl cholesterylxanthate, $C_{27}H_{45}\cdot O\cdot CS\cdot SMe$, is prepared by adding an excess of carbon disulphide to potassium cholesteroxide, and then warming with methyl iodide or sulphate. It crystallises in colourless needles, m. p. 126°, and has $[\alpha]_D$ −39° in 9% toluene solution. When heated, it begins to decompose at 200°, yielding methyl hydrosulphide, carbonyl sulphide, and a hydrocarbon, *cholesterylene*, $C_{27}H_{44}$. This forms colourless needles, m. p. 77°, and has $[\alpha]_D$ −107° in 11% toluene solution. It decolorises bromine, and gives the usual cholesterol reactions.

J. J. S.

Preparation of Cholesteryl α-Bromo*iso*valerate. Chemische Werke vorm. Dr. Heinrich Byk (D.R.-P. 214157).—*Cholesteryl α-bromo*isovalerate, m. p. 132—133°, results from the action of α-bromo-*iso*valeryl chloride on a mixture of cholesterol and diethylaniline in dry benzene; it is insoluble in water, and has no taste. The ester is hydrolysed by aqueous alkalis; these properties render it a valuable therapeutic agent.

F. M. G. M.

Phytosterols in the Family of Synantherea. Faradiol, a New Dihydric Alcohol from Coltsfoot. Timothée Klobb (*Compt. rend.*, 1909, **149**, 999—1001. Compare Abstr., 1903, i, 165; 1904, i, 410; 1905, i, 594).—The following substances have been isolated from the flowers of *Tussilago farfara*: (1) a saturated hydrocarbon, m. p. about 57°; (2) a *phytosterol*, having m. p. about 127°, and forming an *acetate*, m. p. 117—119°, $[\alpha]_D$ −36·7° in chloroform; (3) a viscous, yellow substance; (4) a dihydric alcohol, *faradiol*, $C_{30}H_{50}O_2$ (or $C_{31}H_{52}O_2$ or $C_{29}H_{46}O_2$). This crystallises from alcohol in large,

efflorescent, ortho-rhombic prisms, containing 1 mol. of alcohol and having m. p. 209—211°; after removal of alcohol, m. p. about 238°; $[\alpha]_D$ +45·1° in acetone. It gives Liebermann's reaction, developing a strawberry-red coloration with a green fluorescence. The *acetate* has m. p. 140—145°, $[\alpha]_D$ +63·6°, and appears to exist in two modifications; the *propionate* crystallises in pearly lamellæ, m. p. 155—158°, $[\alpha]_D$ +62·3° in benzene. The *phenylurethane*, $C_{44}H_{60}O_4N_2$, crystallises in prisms, and becomes pasty at 190—205°. W. O. W.

Dehydration of *cyclo*Hexanolpropan-β-ol. P. Joseph Tarbouriech (*Compt. rend.*, 1909, **149**, 862—864. Compare Abstr., 1909, i, 796).—When *cyclo*hexanolpropan-β-ol is heated with sulphuric acid (20%), a *hydrocarbon*, C_9H_{14}, is produced (together with a mixture of polymerides), and a *pinacoline*, $C_9H_{16}O$. The hydrocarbon is a very mobile liquid, b. p. 76°/19 mm. which combines with bromine and forms a *hydrochloride*, b. p. 96—98°/20 mm., and a *dihydrochloride*, b. p. 122—123°/18 mm. The ketone is separated by submitting the mixture to Crismer's method of oximation, when two isomeric compounds are obtained and separated by crystallisation from absolute alcohol; the α-*oxime* has m. p. 83°, the β-*oxime*, m. p. 45°; when these are treated with phenylcarbimide, they form two *carbanilino-oximes*; the α-derivative occurs in silky needles, m. p. 79—80°, the β-derivative forms hard crystals, m. p. 94—95°.

When regenerated from the mixed oximes, the ketone is obtained as a liquid, b. p. 83°/18 mm., having a camphoraceous odour; the α-*semicarbazone* forms needles, m. p. 158°, whilst the β-*semicarbazone* has m. p. 176°.

When the dehydration is effected by anhydrous oxalic acid, the same products are formed, but in different proportions. W. O. W.

New Method of Preparation of Tricyclenecarboxylic Acid (Dehydrocamphenylic Acid). Julius Bredt and R. May (*Chem. Zeit.*, 1909, **33**, 1265).—A 70—80% yield of tricyclenecarboxylic acid is obtained as follows: 50 grams of camphenilic nitrite (compare Jagelki, Abstr., 1899, i, 627) are added in small portions to 250 c.c. of concentrated sulphuric acid at 0°, the resulting product is poured on to 750 grams of ice, and the liquid submitted to steam distillation. The formation of the acid is accompanied by that of two *lactones*, m. p. 137° and 198°. W. H. G.

Preparation of *n*-Propyl *p*-Aminobenzoates. Franz Fritzsche & Co. (D.R.-P. 213459).—The anæsthetic action of the alkyl *m*- and *p*-aminobenzoates is increased by replacing methyl and ethyl with propyl as the ester-forming alkyl group. Further increase in anæsthetic action is not, however, observed when higher alkyl, hydroaromatic, or aromatic groups are employed, but rather an increase in toxicity.

n-Propyl p-*aminobenzoate* is prepared by condensing *n*-propyl alcohol and *p*-nitrobenzoic acid by means of sulphuric acid, and reducing the *n-propyl* p-*nitrobenzoates* with tin and hydrochloric acid; the latter compound forms yellow, rhombic plates, and melts at 35°. The

amino-ester is also produced directly by treating *p*-aminobenzoic acid with *n*-propyl alcohol and either sulphuric acid or hydrogen chloride. It forms needles, m. p. 73—74°. F. M. G. M.

Isomerism by Anils (Schiff's Bases). Wilhelm Manchot and J. R. Furlong (*Ber.*, 1909, 42, 4383—4389).—Whereas ethyl *o*-hydroxybenzylidene-*p*-aminobenzoate exists in two isomeric forms (Abstr., 1909, i, 805), only one form of the corresponding methyl ester can be obtained, and the two isomerides of the free acid could not be separated.

Methyl o-*hydroxybenzylidene*-p-*aminobenzoate* forms colourless, hexagonal crystals, m. p. 145°; they become dark red when heated above 100°, but immediately assume the original faint yellow colour when cooled.

o-*Hydroxybenzylidene*-p-*aminobenzoic acid* forms a mass of yellow or orange-red needles, which consist of almost colourless, hexagonal crystals mixed with more highly-coloured needles. When allowed to crystallise from, or heated with, amyl alcohol above 100°, the crystals become red, but lose their colour on cooling. The solid when heated becomes red at 90°, orange at 160°, sealing-wax red at 220°, bluish-red at 250°; m. p. 259° to a dark red liquid, which on cooling solidifies first to a red and finally to a yellow mass.

When exposed to light it rapidly becomes orange-red, but loses the colour again in the dark. When cooled in liquid air it becomes almost colourless.

The *hydrochlorides* of both yellow and red modifications of ethyl *o*-hydroxybenzylidene-*p*-aminobenzoate, prepared by interaction with hydrogen chloride in boiling benzene solution (yellow form) or in ethereal solution at −15° (red form), are yellow, crystalline precipitates, both m. p. 175—180° and very similar. When powdered with water, however, that from the yellow form regenerates this substance, whilst that from the red product gives a red substance, which becomes yellow at 83°, m. p. 87°. The two hydrochlorides must therefore be regarded as different.

p-*Hydroxy*-m-*methoxybenzylidene*-p-*aminobenzoic acid* is an amorphous substance, m. p. 209°. When heated with water it forms a red oil solidifying to red needles, which when dried lose their crystalline character. The colour vanishes at 75—77°, and the product has m. p. 200°.

Ethyl p-*hydroxy*-m-*methoxybenzylidene*-p-*aminobenzoate* forms glistening, faint yellow plates, m. p. 149°. It gives rise to a red, crystalline substance when treated with water and a little hydrogen chloride. The *hydrochloride* has m. p. 213—217°.

The following anils are also described; in no case were two isomerides obtained:

p-*Hydroxy*-m-*methoxybenzylidene*-o-*toluidine* is colourless, m. p. 115·5°.

p-*Hydroxy*-m-*methoxybenzylidene*-p-*toluidine* crystallises in well-formed, colourless columns, m. p. 117°.

p-*Methylbenzylidene*-p-*aminobenzoic acid* forms colourless crystals, m. p. 241°.

p-iso*Propylbenzylidene*-p-*aminobenzoic acid* yields citron-yellow crystals, m. p. 245°.

3 : 4-*Methylenedihydroxybenzylidene*-p-*aminobenzoic acid* yields a bright yellow, crystalline mass, m. p. 242°.

Benzylidene-p-*aminobenzoic acid* gives colourless crystals, m. p. 193·5°.

p-*Hydroxybenzylidene*-o-*toluidine* has m. p. 169·5°.

Ethyl p-*hydroxybenzylidene*-p-*aminobenzoate* forms a bright yellow or almost colourless mass of glistening plates, m. p. 174·5°. The *methyl* ester separates in almost colourless needles, m. p. 189°.

o-*Methoxybenzylidene*-p-*aminobenzoic acid* forms faintly yellow-coloured crystals, m. p. 227°; the *ethyl* ester has m. p. 106°.

E. F. A.

Synthesis of Aromatic Amino-acids by Rearrangements. III. Alkylaminotoluic Acids. Josef Houben, Arnold Schottmüller, and Robert Freund (*Ber.*, 1909, **42**, 4488—4496).—By the rearrangement, under certain conditions, of phenylcarbamates containing an alkyl group united with the nitrogen into aminobenzoates (compare Abstr., 1904, i, 1014; 1909, i, 921), the authors have succeeded in extending Kolbe's hydroxybenzoic acid synthesis to the corresponding amino-compounds. In the latter case, the yield of amino-acid never exceeds about 40%, and the final reaction must be represented by the equation:

$$2NRPh\cdot MgX + CO_2 = MgX\cdot O\cdot CO\cdot C_6H_4\cdot NR\cdot MgX + NHRPh,$$

where X = halogen, according to which the maximum possible yield is 50%, which has now been nearly approached.

The reaction has been applied to methylamino- and ethylamino-*o*-toluene, both of which give *p*-carboxylic acids, but the highest yields obtained are only about 12%, owing to the sensitiveness of the aminotoluic acids or their salts to the high temperatures at which they are formed. In the syntheses effected with the alkylanilines, considerable proportions of tertiary amino-acids were often obtained, but with the alkyltoluidines, even when large amounts of dialkyltoluidine are added, only the secondary amino-acids are obtained; these can be characterised by conversion into nitroaminic acids, or where this presents complications, into the acetyl derivatives by shaking the aqueous solutions of the alkali salts with acetic anhydride.

In the preparation of the aminotoluic acids, just as with the aniline-carboxylic acids, carbamide-like compounds are always formed in large or small proportion.

A secondary aminotoluic acid is obtained also when, in place of methylamino-*o*-toluene, a mixture of *o*-toluidine and dimethylamino-*o*-toluene is employed, so that either the *o*-toluidine undergoes methylation or the dimethylamino-*o*-toluene, demethylation.

6-*Methylamino*-m-*toluic acid*, $NHMe\cdot C_6H_3Me\cdot CO_2H$, prepared by treating a mixture of *o*-toluidine and *o*-dimethylaminotoluene with magnesium and ethyl iodide in ethereal solution, and subsequently passing carbon dioxide through the liquid, forms long, white needles,

m. p. 201°. *Ditolylmethylcarbamide* (?), $C_6H_4Me\cdot NH\cdot CO\cdot NMe\cdot C_6H_4Me$, also formed in this reaction, has m. p. 238°.

6-*Methylnitrosoamino*-m-*toluic acid*, $NO\cdot NMe\cdot C_6H_3Me\cdot CO_2H$, forms yellow needles, m. p. 153°.

6-*Ethylamino*-m-*toluic acid*, $NHEt\cdot C_6H_3Me\cdot CO_2H$, prepared from *o*-ethylaminotoluene and ethyl iodide, forms white needles, m. p. 169—170°, and gives salts with both alkalis and mineral acids. The *acetyl* derivative, $NEtAc\cdot C_6H_3Me\cdot CO_2H$, has m. p. 228°. 6-*Ethylnitrosoamino*-m-*toluic acid*, $NO\cdot NEt\cdot C_6H_3Me\cdot CO_2H$, forms long, yellow needles, m. p. 135°. The *diethylditolylcarbamide* (?),

$$CO(NEt\cdot C_6H_4Me)_2,$$

formed together with 6-ethylamino-*m*-toluic acid, forms long, white needles, and carbonises on heating.

4-*Ethylamino*-m-*toluic acid*, $NHEt\cdot C_6H_3Me\cdot CO_2H$, prepared from *p*-ethylaminotoluene and ethyl iodide, crystallises in yellow leaflets, m. p. 191°. The contiguity of the ethylamino- and carboxyl groups is indicated by the intense, bluish-violet fluorescence (similar to that shown by anthranilic acid) exhibited by aqueous and alcoholic solutions of the acid; this fluorescence disappears on addition of dilute acetic acid, apparently owing to salt formation, the basicity of the ethylamino-group being possibly increased by the methyl group in the para-position. The corresponding *nitroso-acid*, m. p. 184° (impure), was obtainable only in small quantity. The ethylaminotoluic acid is accompanied by *ditolylethylcarbamide* (?),

$$C_6H_4Me\cdot NH\cdot CO\cdot NEt\cdot C_6H_4Me,$$

m. p. 283°. T. H. P.

Addition of Ethyl Phenylacetate to Unsaturated Compounds. Walther Borsche (*Ber.*, 1909, 42, 4496—4499).—In the author's investigations on the reactivity of the methylene group in the nitro-derivatives of ethyl phenylacetate (Abstr., 1909, i, 233, 385), it was found that these compounds do not readily form additive compounds with ethylene linkings. Sodium ethoxide attacks them rapidly, with destruction of the methylene group, whilst, under the influence of piperidine at 100°, addition occurs very slowly and imperfectly. With ethyl phenylacetate itself, however, in spite of its slight reactivity compared with the nitro-derivatives, addition takes place readily with $\alpha\beta$-unsaturated ketones and carboxylic esters in presence of sodium ethoxide. If ketones containing a methylene group are employed, ring-closure with loss of alcohol occurs under the influence of the sodium ethoxide, the resulting compounds being phenyl derivatives of dihydroresorcinol.

Ethyl $\alpha\beta$-*diphenylglutarate*, $CO_2Et\cdot CHPh\cdot CHPh\cdot CH_2\cdot CO_2Et$, prepared from ethyl phenylacetate and ethyl cinnamate, forms colourless needles, m. p. 92—93°. The free *acid*, $C_{17}H_{16}O_4$, forms colourless needles, m. p. 230—231°.

The nitrile of α-phenylcinnamic acid does not form an additive compound with ethyl phenylacetate under the conditions employed.

Ethyl γ-*benzoyl*-$\alpha\beta$-*diphenylbutyrate*, $CO_2Et\cdot CHPh\cdot CHPh\cdot CH_2Bz$, prepared from ethyl phenylacetate and benzylideneacetophenone,

forms white, silky needles, m. p. 153—154°; the corresponding *acid* is obtained as a white powder, m. p. about 240°.

2-*Phenyl*-1 : 1-*dimethyl*cyclo*hexan*-3 : 5-*dione*,

$$CMe_2<\begin{matrix}CH_2\text{---}CO\\CHPh\cdot CO\end{matrix}>CH_2,$$

prepared from ethyl phenylacetate and mesityl oxide, forms colourless leaflets containing $1H_2O$, m. p. about 135° (anhydrous).

1 : 2-*Diphenyl*cyclo*hexan*-3 : 5-*dione*, $CHPh<\begin{matrix}CH_2\text{---}CO\\CHPh\cdot CO\end{matrix}>CH_2$, obtained, together with a resinous polymeride of benzylideneacetone, by the interaction of the latter and ethyl phenylacetate, forms colourless leaflets, m. p. 159—160°. T. H. P.

allo- and *iso*-Cinnamic Acids. Carl Liebermann and H. Trucksäss (*Ber.*, 1909, 42, 4659—4674. Compare Abstr., 1909, i, 155; also Biilmann, *ibid.*, i, 155, 382).—The authors give full particulars of the precautions necessary when working with one of these acid in order to avoid inoculation with particles of one of the isomeric acids. The hands, corks, and filter-papers are washed with alcohol and ether, and all glass vessels are "sterilised" by heating for some time at 105°.

In the preparation of the *iso*-acid, m. p. 42°, by fusing the *allo*-acid at 105°, and cooling in a flask fitted with a sterile cork, it is an advantage to work with small amounts (0·5 gram) at a time, since, with larger quantities, it is more difficult to destroy all particles of the *allo*-acid, and on solidification the minute particles left cause the separation of crystals of *allo*-acid. The *iso*-acid can be crystallised from light petroleum, b. p. 30—50°, or even b. p. 60—70° if proper precautions are taken. The acid is characterised by its rhombic crystals, their elastic nature, the soapy feel of the crystals when rubbed with a pestle, and their planes of cleavage.

No trustworthy method of obtaining the *iso*-acid, m. p. 58°, without inoculation with a particle of the acid is known.

The three acids when converted into calcium salts by shaking with water and powdered marble, and then precipitated with dilute hydrochloric acid, gave the original acid. This may be due to the fact that small particles of the original acid were not transformed into the calcium salt, and when acidified served as nuclei which produced the separation of the acid in question.

The three acids were converted into aniline salts; in each case the aniline salt had the same m. p., namely, 83—84° (Erlenmeyer, sen., Abstr., 1896, i, 46). The acid was recovered from the aniline salt by the following three methods: 1. Precipitation of the hot aqueous solution of the salt with excess of hydrochloric acid, filtering and washing the precipitate, and extracting the mother liquor with ether. 2. Rubbing the dry salt with very dilute hydrochloric acid and extracting with ether. 3. Rubbing the salt with dilute alkali, removing the aniline with ether, acidifying the alkaline liquid, and extracting the acid with ether.

By the first method, all three acids gave the *iso*-acid, m. p. 58°, with

the exception of one experiment, when the *iso*-acid, m. p. 42°, was obtained. Method 2 gave varying results. Method 3 gave either *allo*-acid or *iso*-acid, m. p. 42°.

The *iso*-acid, m. p. 58°, and the *allo*-acid can be converted into the *iso*-acid, m. p. 42°, by boiling with very dilute hydrochloric acid, and cooling in a flask provided with a cotton-wool plug.

One of the best methods of transforming the *allo*-acid or *iso*-acid, m. p. 58°, into the more fusible *iso*-acid is to dissolve in excess of sodium hydroxide solution, and, after two hours, to precipitate with hydrochloric acid (D 1·1). If precautions are taken, the acid which separates is always the *iso*-acid, m. p. 42°. J. J. S.

Bromination of *o*-Nitrophenylpropiolic Acid. Gustav Heller and Walter Tischner (*Ber.*, 1909, **43**, 4566—4568).—By the action of bromine vapour, or of an excess of bromine in benzene on *o*-nitrophenylpropiolic acid, *αβ-dibromo-o-nitrocinnamic acid*,

$$NO_2 \cdot C_6H_4 \cdot CBr{:}CBr \cdot CO_2H,$$

is formed in small quantity mixed with nitrocinnamic acid. The dibromo-acid crystallises in stellate aggregates of colourless, lustrous needles, m. p. 222° (decomp.).

Bromination in glacial acetic acid solution leads to the formation of *aaββ-tetrabromo-o-nitrophenylethane*, $NO_2 \cdot C_6H_4 \cdot CBr_2 \cdot CHBr_2$, which crystallises in rectangular, glistening, yellow plates, m. p. 186°.

E. F. A.

Preparation of *o*-ω-Trichloroacetoxybenzoic Acid. Chemische Fabrik von Heyden (D.R.-P. 213591. Compare Abstr., 1909, i, 798). —*o*-ω-*Trichloroacetoxybenzoic acid*, $CO_2H \cdot C_6H_4 \cdot O \cdot CO \cdot CCl_3$, can be prepared by treating salicylic acid or its salts with trichloroacetic anhydride or trichloroacetyl chloride in the presence of a tertiary base, such as dimethylaniline. It forms colourless crystals, m. p. 150—152°. The acid chloride or anhydride can be replaced by the free acid if phosphorus trichloride or phosphoric oxide is also employed. The chlorination of *o*-acetoxybenzoic acid leads to substitution in the phenyl nucleus instead of in the side-chain.

F. M. G. M.

Preparation of Aromatic Halogenalkyloxycarboxylic Acids. Chemische Fabrik von Heyden (D.R.-P. 213593).—It has been found that when the tolyl halogen alkyl ethers are oxidised with either permanganate, manganese dioxide with sulphuric acid, or dichromate and sulphuric acid they yield the corresponding carboxylic acids without any loss of halogen from the alkyloxy-group.

p-*Bromoethoxybenzoic acid*, $CO_2H \cdot C_6H_4 \cdot O \cdot C_2H_4Br$, colourless, glistening leaflets, m. p. 178°, is thus prepared from *p*-tolyl bromoethyl ether; the *ethyl* ester has m. p. 76°.

o-*Bromoethoxybenzoic acid*, from *o*-tolyl bromoethyl ether, melts at 164°. F. M. G. M.

Preparation of *o*-Thymotic Acid and of Certain of its Derivatives. Rosario Spallino and G. Provenzal (*Gazzetta*, 1909, 39, ii, 325—336).—By the action of sodium on a xylene solution of thymol through which a current of carbon dioxide was passed, the author has prepared *o*-thymotic acid, which forms monoclinic crystals [Rosati, $a:b:c=1{\cdot}0724:1:0{\cdot}9039$; $\beta=93°24'$], m. p. 127°. Kolbe and Lautemann (*Annalen*, 1860, 115, 205) and Kobek (Abstr., 1884, 56) gave 120°, and Puxeddu (Abstr., 1906, i, 995), 123°. The *silver* and *sodium* salts were prepared; the *methyl* ester,

$$CPr\langle\begin{matrix}CH\text{———}CH\\C(OH):C(CO_2Me)\end{matrix}\rangle CMe,$$

b. p. 142°/18·5 mm., and the *ethyl* ester, $C_{13}H_{18}O_3$, b. p. 153°/18·5 mm., are pale yellow, oily liquids.

The action of phosphoric oxide or phosphoryl chloride on *o*-thymotic acid in xylene solution yields a mixture of two isomeric thymotides (compare Naquet, *Bull. Soc. chim.*, 1863, 4, 96; 1865, 6, 98). The *first*, $C_{22}H_{24}O_4$, forms colourless, rhombohedral crystals (Rosati, $a:c=1:1{\cdot}1092$; $\alpha=94°11'$], m. p. 174°, and is hydrolysed readily by alcoholic potassium hydroxide, and more slowly by concentrated sulphuric acid, yielding *o*-thymotic acid; the *second* isomeride, m. p. 209°, forms biaxial crystals, and is readily hydrolysed by alcoholic potassium hydroxide or concentrated sulphuric acid. The two thymotides exhibit different solubilities in various solvents, but both give normal molecular weights in freezing benzene or phenol. They are probably stereoisomerides of the structure: $\begin{matrix}CH{:}CMe\cdot C\cdot CO\cdot O\cdot C\cdot CPr{=}CH\\ \quad\|\qquad\qquad\|\qquad\quad\|\\CH{=}CPr\cdot C\cdot O\cdot CO\cdot C\cdot CMe{:}CH\end{matrix}$.

T. H. P.

Action of Free Hydroxylamine on Coumarin. Luigi Francesconi and Guido Cusmano (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 183—188).—The authors traverse the statement made by Posner (Abstr., 1909, i, 583) that the dihydroxylaminohydrocoumarin described by them (*ibid.*, i, 233) is a mixture of β-hydroxylaminodihydrocoumarohydroxamoxime hydroxide and β-aminodihydrocoumaric acid (termed aminohydrocoumaric acid by the present authors).

Further experiments show that at 0° coumarin takes up 3 mols. of hydroxylamine, giving β-hydroxylaminodihydrocoumarohydroxamoxime hydroxide, m. p. 123°. At the ordinary temperature (20—25°), that is, under the conditions in which 1 mol. of hydroxlamine is added to the lactonic linking of santonin, only 2 mols. of hydroxylamine are added to coumarin, the resultant product being dihydroxylaminohydrocoumarin, m. p. 130—131°, which is far more stable than β-hydroxylaminodihydrocoumarohydroxamoxime hydroxide. At the b. p. of methyl alcohol, either no reaction occurs or aminohydrocoumaric acid is formed. T. H. P.

Anhydrides of *iso*Phthalic and Terephthalic Acids. John E. Bucher and W. Clifton Slade (*J. Amer. Chem. Soc.*, 1909, 31, 1319—1321).—It has been stated in certain well known text-books that *iso*phthalic and terephthalic acids cannot form anhydrides. It

has been found, however, that the anhydrides of both acids can be obtained by dissolving the acids in acetic anhydride and distilling off the liquid at 200°. The *anhydrides* are thus obtained as granular substances, which decompose on heating without showing definite m. p., are not volatile, and are readily soluble in warm solutions of alkali hydroxides. The properties of these compounds indicate that they have a high molecular weight, and may be represented by the formula $[C_6H_4(CO)_2O]_x$. E. G.

β-Phenylglutaconic Acid. Franz Feist and G. Pomme (*Annalen*, 1909, **370**, 72—81. Compare this vol., i, 7).—β-Phenylglutaconic acid, prepared by any one of the known methods (compare Michael, Abstr., 1894, i, 172; Ruhemann, Trans., 1899, **75**, 248; Buchner and Schroeder, Abstr., 1902, i, 319), is obtained in one modification only, m. p. 154—155°, which is regarded by Buchner and Schroeder as the *cis*-form, because of its close relationship to the anhydride; this view, however, is shown to be incorrect; the acid, m. p. 154—155°, must have the *trans*-configuration, for the anhydride when acted on by alkali in the presence of casein yields on precipitation with silver nitrate a silver salt, which, when suspended in ether and decomposed by hydrogen sulphide, yields the anhydride, whereas, in the absence of casein, the acid, m. p. 154°, is obtained; the presence of the anti-catalyst prevents the transformation of the labile *cis*-isomeride into the *trans*-acid, but the former, being unstable, passes into the anhydride. The crystalline *barium* and *calcium* salts were analysed. The *semi-anilide*, $C_{17}H_{15}O_3N$, prepared from the anhydride and aniline, forms pearly crystals, m. p. 174°; the *barium* salt,

$$(C_{17}H_{14}O_3N)_2Ba,4H_2O,$$

was analysed; the corresponding *semi*-p-*toluidide*, $C_{18}H_{17}O_3N$, forms aggregates of pearly crystals, m. p. 184°. The *anil*,

$$CPh\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}CH{-}CO\\ CH_2{\cdot}CO\end{matrix}\begin{matrix}>\\ \\ \end{matrix}NPh,$$

obtained by the action of aniline on the acid at 130°, crystallises in colourless needles, m. p. 232°; the corresponding p-*tolil*, $C_{18}H_{15}O_2N$, crystallises in needles, m. p. 248·5—249°.

β-Phenyl-α-benzylglutaconic acid, $CO_2H{\cdot}CH(CH_2Ph){\cdot}CPh{:}CH{\cdot}CO_2H$, prepared by the action of benzyl chloride and sodium ethoxide on ethyl β-phenylglutaconate at 110° under pressure, is an oil; the *barium* and *silver* salts were analysed.

Ethyl β-phenylglutaconate, when heated with benzaldehyde and an alcoholic solution of potassium hydroxide, yields *β-phenyl-α-benzylideneglutaconic acid*, $CO_2H{\cdot}C(:CHPh){\cdot}CPh{:}CH_2{\cdot}CO_2H$, crystallising in compact needles, m. p. 210·5°.

β-Phenylglutaconic acid does not combine with hydrogen bromide, but absorbs bromine slowly, yielding *αβ-dibromo-β-phenylglutaric acid*, $CO_2H{\cdot}CHBr{\cdot}CPhBr{\cdot}CH_2{\cdot}CO_2H$, which forms crystals, m. p. 166° (decomp.). W. H. G.

Action of Sulphuric Acid on Santonin. II. Guido Bargellini and S. Silvestri (*Gazzetta*, 1909, **39**, ii, 346—349. Compare Abstr., 1909, i, 723).—The authors have investigated the products obtained

by the action of sulphuric acid (D 1·5) on santonin at various temperatures. At the ordinary temperature (about 20°), *l*-desmotroposantonin is formed; at 30—50°, a mixture of *l*-desmotroposantonin and desmotroposantonin, and at 50—90°, a mixture of desmotroposantonin, $[\alpha]_D$ + 112°, *d*-santonous acid, and a red, tarry matter. At 100°, no desmotroposantonin is formed, the product consisting entirely of *d*-santonous acid and the red tar. Desmotroposantonin is converted into these two substances by the action of sulphuric acid (D 1·5) at 100°, and hence forms the first product of the action of the acid on santonin, its conversion into santonous acid by reduction being probably accompanied by a corresponding oxidation to a ketosantonous acid, thus: $:CH\cdot OH + H_2 = H_2O + :CH_2$ (santonous acid) and $:CH\cdot OH + O = H_2O + :CO$ (ketosantonous acid). The red, tarry matter is being investigated in order to ascertain whether it contains a ketosantonous acid.

The action of syrupy phosphoric acid (D 1·725) on santonin is similar to that of sulphuric acid (D 1·5). T. H. P.

Benzaldehydesulphoxylates. Max Bazlen (*Ber.*, 1909, **42**, 4634—4637. Compare Abstr., 1905, ii, 240).—In reply to Fromm and Erfurt (Abstr., 1909, i, 936), the author gives full details for the preparation of sodium benzaldehydesulphoxylate, $NaHSO_2,C_6H_5\cdot CHO$, from sodium hyposulphite, sodium hydroxide solution, and benzaldehyde. The yield is almost theoretical, and the product can be crystallised from hot water containing a little sodium hydroxide, when it forms well developed crystals. The analogous *zinc* compound, $Zn(HSO_2,C_6H_5\cdot CHO)_2,4H_2O$, can be obtained by shaking benzaldehyde with a warm solution of zinc hyposulphite. It also forms well developed crystals. These primary salts are very unstable in contact with the air. Secondary salts have also been prepared, and are more stable. *Disodium benzaldehydesulphoxylate*, $Na_2SO_2,C_6H_5\cdot CHO,2H_2O$, forms colourless needles, and can be obtained by the action of sodium hydroxide solution on the primary sodium salt. The *barium* and *zinc* salts have been prepared. J. J. S.

Preparation of *p*-Methoxysalicylaldehyde from *p*-Hydroxysalicylaldehyde. Kalle & Co. (D.R.-P. 214153).—*p*-Methoxysalicylaldehyde was only obtained in small yield from resorcinol monomethyl ether by the Tiemann reaction owing to its instability. It has now been found possible to prepare it in a stable, pure condition by methylating *p*-hydroxysalicylaldehyde with methyl sulphate or methyl halide at 70—80° in the presence of aqueous sodium carbonate. The pure product melts at 41°, not at 62—63°, and, contrary to the statements in the literature, is readily soluble in water, particularly on warming. F. M. G. M.

New Syntheses of Vanillin. Alfred Guyot and A. Gry (*Compt. rend.*, 1909, **149**, 928—931. Compare Abstr., 1909, i, 236, 306, 935).—An application of the general method for the preparation of aldehydes described previously (Abstr., 1909, i, 935) to the synthesis of vanillin. The following compounds are prepared by the

condensation of mesoxalic esters or of $\alpha\beta$-diketonic esters with guaiacol.

Methyl p-*hydroxy*-m-*methoxyphenyltartronate*, $OMe{\cdot}C_6H_3(OH){\cdot}C(OH)(CO_2Me)_2$, prisms, m. p. 115°; the *ethyl* ester crystallises in long needles, m. p. 64°. *Ethyl* p-*hydroxy*-m-*methoxyphenylacetylglycollate*, $C_7H_7O_2{\cdot}CAc(OH){\cdot}CO_2Et$, prisms, m. p. 61°. *Ethyl* p-*hydroxy*-m-*methoxyphenylbenzoylglycollate*, $C_7H_7O_2{\cdot}CBz(OH){\cdot}CO_2Et$, prisms, m. p. 139°.

The esters are converted into vanilloylcarboxylic acid by one of the methods mentioned previously (*loc. cit.*). A quantitative yield of pure vanillin is obtained when the acid is heated at 170° with an equal weight of dimethyl-*p*-toluidine (compare Gassmann, Abstr., 1907, i, 343).

The $\alpha\beta$-diketonic esters employed in this synthesis can be replaced by the corresponding acids. The yield of vanillin, however, is diminished, thus dihydroxytartaric acid gave only 15% of the weight of guaiacol employed. W. O. W.

Organic Syntheses by Means of Sunlight. IV. Action of Paraffins and Homologues of Benzene on Ketones and Aldehydes. Emanuale Paternò and G. Chieffi (*Gazzetta*, 1909, 39, ii, 415—435. Compare Abstr., 1909, i, 393, 487).—The interaction of benzophenone and pentane under the influence of sunlight results in the formation of benzopinacone and a resin, which may be a polymeride of the characteristic compound of benzophenone and amylene (*loc. cit.*).

Benzophenone and octane yield benzopinacone and a resin, which was not identified.

Benzophenone and decane (di*iso*amyl) give benzopinacone and a resinous *additive* compound, $C_{13}H_{10}O,C_{10}H_{20}$.

In general, then, aliphatic hydrocarbons are transformed by the action of benzophenone into unsaturated hydrocarbons, which yield additive compounds with the benzophenone: $3C_{13}H_{10}O + C_nH_{2n+2} = C_{26}H_{22}O_2 + C_{13}H_{10}O,C_nH_{2n}$; these additive compounds are resins, and are decomposed into their constituents on heating.

Benzaldehyde and pentane yield hydrobenzoin (?) and polymerides of benzaldehyde, similar results being obtained with benzaldehyde and octane or decane and with *p*-tolualdehyde and octane.

With certain cyclic hydrocarbons, such as *cyclo*hexane or methyl- or dimethyl-*cyclo*hexane, benzophenone yields benzopinacone and a resin which has not yet been investigated.

Benzophenone and benzene do not seem to react under the influence of sunlight. Benzophenone and toluene yield benzopinacone and an *additive* compound, $C_{20}H_{18}O$, m. p. 79—82°, probably analogous to that formed by benzophenone and benzyl alcohol (compare Hell and Wiegandt, Abstr., 1904, i, 490).

Benzophenone and ethylbenzene give: (1) benzopinacone; (2) a *compound*, m. p. 87—89°, probably $OH{\cdot}CPh_2{\cdot}CH_2{\cdot}CH_2Ph$, which has the normal molecular weight in freezing benzene, and, when

treated with phosphoric oxide, yields the *triphenylpropylene*, $CPh_2{:}CH{\cdot}CH_2Ph$, m. p. 87—89°; (3) a hydrocarbon, m. p. 124—125°, probably dimethyldibenzyl (compare Moritz and Wolffenstein, Abstr., 1899, i, 424).

Benzophenone and propylbenzene yield benzopinacone and a *compound*, $C_{13}H_{10}O,C_9H_{12}$ (or $C_{13}H_{10}O,C_9H_{10}$), m. p. 94—96°, which, with phosphoric oxide, gives an *anhydride*, m. p. 80—81° and not a hydrocarbon.

Benzophenone and *p*-xylene give benzopinacone and di-*p*-methyldibenzyl (compare Moritz and Wolffenstein, Abstr., 1899, i, 910).

Benzophenone and cymene yield benzopinacone, a hydrocarbon with an unsaturated chain, and a resin, now under examination.

Benzophenone and oil of turpentine give benzopinacone and a viscous oil, b. p. 280—320°, which yields benzophenone on distillation.

Benzophenone and diphenylmethane yield *aaββ*-tetraphenylethanol, $CHPh_2{\cdot}CPh_2{\cdot}OH$, which forms monoclinic crystals [Zambonini: $a:b:c = 2{\cdot}9673:1:3{\cdot}0298$; $\beta = 91°50'$], m. p. 212—214°, and has the normal molecular weight in boiling alcohol or benzene; when treated with phosphoric oxide, or with phosphorus and iodine, it yields *s*-tetraphenylethane.

With benzaldehyde and toluene, dibenzyl or diphenylmethane, no reaction occurs, the benzaldehyde undergoing rapid polymerisation. Anisaldehyde and toluene yield hydroanisoin and a resin, not yet examined. With oil of turpentine and benzaldehyde, *iso*hydrobenzoin is formed. T. H. P.

2 : 4 : 6-Tribromobenzophenone. P. J. Montagne (*Rec. trav. chim.*, 1909, **28**, 449—455. Compare Abstr., 1908, i, 988).—It is shown that the yellow product formed when 2 : 4 : 6-tribromobenzophenone is heated is 6 : 8-dibromofluorenone. 2 : 4 : 6-Tribromobenzophenone is reduced to 4-bromobenzhydrol when heated with sodium hydroxide in alcohol. The latter reaction to some extent negatives the suggestion of Diels and Rhodius (Abstr., 1909, i, 351), that since the carbonyl group of ketones is reduced by sodium amyloxide, but not by sodium ethoxide, some specific action must be exerted by the amyl group in the former reagent. The author finds in fact that benzophenone is readily reduced either by potassium hydroxide or sodium hydroxide in alcohol.

6 : 8-*Dibromofluorenone*, m. p. 225°, b. p. 430° (decomp.), crystallises in slender needles from alcohol; on reduction with sodium amalgam it yields fluorene alcohol, and on oxidation with sulphuric acid and mercuric sulphate, it furnishes phthalic anhydride. T. A. H.

Derivatives of Catechol. Hugo Voswinckel (*Ber.*, 1909, **42**, 4651—4654. Compare Dreczgowski, *J. Russ. Phys. Chem. Ges.*, 1893, **25**, 157).—Chloroacetocatechol diacetate, $C_6H_3(OAc)_2{\cdot}CO{\cdot}CH_2Cl$, has m. p. 110°, not 95°, and 3 : 4-diacetoxyacetophenone, m. p. 87°, not 78°.

In the preparation of chloroacetocatechol a small amount of a higher condensation product, $C_2H_4[CO\cdot C_6H_3(OH)_2]_2$ or

$$C_6H_2(OH)_2<\begin{matrix}CO\cdot CH_2\\ CH_2\cdot CO\end{matrix}>C_6H_2(OH)_2,$$

is obtained when phosphoryl chloride is used. It crystallises in glistening, silver, hexagonal plates, m. p. 261°. Its *tetra-acetyl* derivative, $C_{24}H_{20}O_{10}$, crystallises from nitrobenzene in rhombic plates, m. p. 253°.

3 : 4 : *α-Triacetoxyacetophenone*, $C_6H_3(OAc)_2\cdot CO\cdot CH_2\cdot OAc$, obtained by heating chloroacetocatechol (α-chloro-3 : 4-dihydroxyacetophenone) with acetic anhydride and dry potassium acetate, crystallises in plates, m. p. 94°, and when hydrolysed with alcoholic sodium hydroxide solution yields 3 : 4-*α-trihydroxyacetophenone*,

$$C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot OH,$$

which crystallises in colourless prisms, m. p. 195°. When reduced with zinc dust and glacial acetic acid, the triacetoxy-derivative yields 3 : 4-*diacetoxyphenylethyl acetate*, $C_6H_3(OAc)_2\cdot CH_2\cdot CH_2\cdot OAc$, which crystallises in colourless plates, m. p. 85°. When heated with acetic anhydride and potassium acetate, or when heated alone at 130°, the triacetoxy-derivative yields 3 : 4-*diacetoxyphenylacetaldehyde*,

$$C_6H_3(OAc)_2\cdot CH_2\cdot CHO,$$

and acetaldehyde. The former crystallises in large, thin plates, m. p. 88°, and yields a crystalline *phenylhydrazone*. J. J. S.

Relationship between the Colour and Constitution of Unsaturated Ketones and Their Salts. Hans Stobbe (*Annalen*, 1909, **370**, 93—99).—A brief account of the nature and results of the investigations described in the following papers. W. H. G.

Light Absorption, Basicity, Constitution, and Salts of Ketones of the Dibenzylideneacetone [Distyryl Ketone] and Dibenzylidene*cyclo*pentanone Series. Hans Stobbe and Richard Haertel (*Annalen*, 1909, **370**, 99—129).—I. *Colour of Ketones of the Dibenzylideneacetone and Dibenzylidene*cyclo*pentanone Types.*—The absorption spectra of *N*/32 solutions of ketones of the types

$$CHR{:}CH\cdot CO\cdot CH{:}CHR'$$

and $\begin{matrix}CH_2\cdot C(:CHR)\\ CH_2\cdot C(:CHR')\end{matrix}>CO$ in chloroform have been measured, where RR′ = benzylidene, 4-methoxybenzylidene, cuminylidene, 2-ethoxybenzylidene, 3 : 4-dimethoxybenzylidene, piperonylidene, cinnamylidene, or furfurylidene; R = benzylidene and R′ = 4-methoxybenzylidene, or R = benzylidene and R′ = piperonylidene.

The results obtained may be summarised thus: (1) The absorption band is shortest when RR′ = benzylidene. (2) Each replacement of a phenyl hydrogen atom by an alkyl or alkyloxy-group is accompanied by an increase in the length of the absorption band; the influence exerted in the ortho-position is smaller than in the para-position; the compounds in which RR′ = 3 : 4-dimethoxybenzylidene and piperonylidene have the greatest absorption. (3) Stereoisomerides, such as the stereoisomeric benzylideneanisylidene*cyclo*pentanones (compare Abstr., 1909, i, 309), exhibit different absorption. (4) The colour intensity

is increased by the addition of ethylene linkings; thus, replacement of benzylidene by cinnamylidene is accompanied by a great increase in the length of the absorption band. (5) Comparison of the spectra of the corresponding acetone and *cyclo*pentanone compounds shows that the absorption bands of the latter are about 10$\mu\mu$ longer than those of the former.

Di-3 : 4-*dimethoxystyryl ketone*, $[C_6H_3(OMe)_2\cdot CH{:}CH]_2CO$, prepared by the interaction of 3 : 4-dimethoxybenzaldehyde and acetone in a dilute alcoholic solution of sodium hydroxide, forms golden-yellow crystals, m. p. 84°. *Di*-2-*ethoxybenzylidene*cyclo*pentanone*, $C_{23}H_{24}O_3$, prepared in a similar manner, has m. p. 110°; the corresponding *di*-3 : 4-*dimethoxybenzylidene* compound, $C_{23}H_{24}O_5$, has m. p. 195·5°.

Benzaldehyde, piperonaldehyde, and *cyclo*pentanone interact in a dilute alcoholic solution of sodium hydroxide, yielding two stereoisomeric *benzylidenepiperonylidene*cyclo*pentanones*,

$$\begin{matrix} CH_2\cdot C(CH\cdot C_6H_3{:}O_2{:}CH_2) \\ | \qquad\qquad\qquad\qquad >CO, \\ CH_2\text{———}C(CHPh) \end{matrix}$$

obtained as lemon-yellow crystals, m. p. 176°, and deep lemon-yellow crystals, m. p. 192°, respectively.

II. *Colour of the Crystalline Chloro-, Dichloro-, and Trichloro-acetates of the Ketones.*—The colour relationship existing between the ketones is found to exist also between the salts. The acid salts are more intensely coloured than the neutral salts. The colour intensity also increases with the strength of the acid. In the following list of salts, K represents one mol. of the ketone and A one mol. of the acid.

Distyryl ketone trichloroacetate, KA, lemon-yellow, m. p. 117°; *dichloroacetate*, KA, pale yellow.

Di-4-*methoxystyryl ketone trichloroacetate*, KA, vermilion, m. p. 93°; K2A, carmine, m. p. 63°; *dichloroacetate*, KA, orange-yellow, m. p. 96°; K2A, orange-red, m. p. 92°; *chloroacetate*, K4A, orange-yellow, m. p. 45°.

Di-2-*ethoxystyryl ketone dichloroacetate*, K2A, orange-red, m. p. 33°.

Di-3 : 4-*dimethoxystyryl ketone trichloroacetate*, KA, brown, m. p. 105°; *dichloroacetate*, KA, orange-yellow, m. p. 87°.

Dipiperonylideneacetone trichloroacetate, K2A, garnet-red, m. p. 87°; *dichloroacetate*, KA, light brown, m. p. 100°.

Styryl 4-*methoxystyryl ketone trichloroacetate*, KA, orange-red, m. p. 66°; *dichloroacetate*, KA, light yellow, m. p. 48°.

Dicinnamylideneacetone trichloroacetate, K2A, black, m. p. 110°; *dichloroacetate*, K2A, very dark red, m. p. 56°; *chloroacetate*, K6A, orange-yellow, m. p. 56°.

*Dibenzylidene*cyclo*pentanone trichloroacetate*, K2A, straw-yellow, m. p. 98°; *dichloroacetate*, KA, sulphur-yellow, m. p. 110°; *chloroacetate*, sulphur-yellow, m. p. 75°.

Di-4-*methoxybenzylidene*cyclo*pentanone trichloroacetate*, K2A, garnet-red, m. p. 73°; *dichloroacetate*, KA, orange-yellow, m. p. 133°; K2A, scarlet, m. p. 85°; *chloroacetate*, K5A, orange-red, m. p. 48°.

*Dipiperonylidene*cyclo*pentanone trichloroacetate*, K4A, black, m. p. 85—90°; KA, orange, m. p. 148°.

*Benzylideneanisylidene*cyclo*pentanone*, m. p. 147°; *trichloroacetate*,

K2A, lemon-yellow, m. p. 97°; *dichloroacetate*, KA, lemon-yellow, m. p. 68°.

*Dicinnamylidene*cyclo*pentanone trichloroacetate*, K2A, black, m. p. 89°; *dichloroacetate*, KA, orange-red, m. p. 158°.

*Difurfurylidene*cyclo*pentanone trichloroacetate*, K2A, black, m. p. 82°; *dichloroacetate*, KA, orange-red, m. p. 158°.

III. *Colour and Composition of the Hydrochlorides of the Ketones at* 15° *and* −75°.—The absorption of hydrogen chloride by the solid ketone has been investigated with the following results: (1) As a rule, at 15°, 1—2 mols., and at −75°, 4—6 mols., of hydrogen chloride are absorbed; the alkyloxy-derivatives combine with a greater proportion of hydrogen chloride than the alkyl compounds; stereoisomerides combine with the same amount of hydrogen chloride. (2) The relationships between colour and constitution observed in the case of the salts with the chloroacetic acids also exist in the case of the hydrochlorides.

IV. *Absorption Spectra of Certain Salts of the Ketones dissolved in Various Acids.*—The absorption spectra of equivalent solutions of the various ketones in sulphuric, phosphoric, chloroacetic, dichloroacetic, trichloroacetic, formic, and acetic acids, and in chloroform have been measured. It is found that the colour of solutions of the same ketone becomes more intense as the strength of the acid increases; the solutions in acetic acid are of approximately the same intensity as in chloroform, indicating the presence of only traces of acetate. It is clear that the colour of the solution depends, not only on the specific colour of the salt, but also to a great extent on the degree of hydrolysis of the salt. The effect of the constitution of the ketone on the colour of the solution remains more or less constant.

V. *Relationship between Basicity of the Ketone and the Colour of Certain Salts of the Ketones.*—The basicity of the various ketones has been determined. It is found that (1) derivatives of dibenzylideneacetone and dibenzylidene*cyclo*pentanone, obtained by substituting phenyl hydrogen atoms, are more basic than the parent substances; *iso*propyl has the smallest effect; dioxymethylene (CH_2O_2·), ethoxy- (EtO·), and methoxy- (MeO·) groups increase the basicity in the order given; the basic character is also increased by substituting furyl and cinnamenyl for phenyl; (2) the basicity of a *cyclo*pentanone compound is about two-thirds of that of the corresponding acetone compound; (3) replacement of benzylidene by *p*-methoxybenzylidene and piperonylidene increases the basicity by 2·4 and 1·7 times respectively; the basicity is roughly doubled by replacing one benzylidene group by a cinnamenyl group; (4) a relationship appears to exist between the light absorption and basicity of the ketones. W. H. G.

Light Absorption, Basicity, Constitution, and Salts of Certain Unsaturated Cyclic Ketones, Ketone Acids, and Ketone-Esters. Hans Stobbe and Siegfried Seydel (*Annalen*, 1909, 370, 129—141).—An investigation on the colour relationships existing between fluorenone, fluorenone-4-carboxylic acid, and ethyl fluorenone-4-carboxylate; *allo*chrysoketonecarboxylic acid and the ethyl ester; dibromoindone, phenylindoneacetic acid, and the ethyl ester.

Fluorenone is lighter in colour than the carboxylic ester, and this again lighter than the acid. The solutions of these substances in sulphuric, trichloroacetic, dichloroacetic, and chloroacetic acids are red or dark yellow, the intensity of the solution of the same substance increasing with the strength of the acid. The solutions of the three compounds in the same acid are of unequal colour-tone, and, unlike the free substances, the solution of the ketone is darker than that of the ester, and this darker than the solution of the acid. The explanation of this is, that the ketone is more basic than the ester, which is more basic than the acid.

The other ketonic substances investigated were found to give the same results; the intensity of the solution in an acid depends both on the strength of the acid and the basicity of the ketone.

Ethyl fluorenone-4-carboxylate crystallises with $2C_6H_6$ in large, sulphur-yellow prisms, m. p. 227°.

Methyl phenylindoneacetate, $C_{18}H_{14}O_3$, forms golden-yellow needles, m. p. 108·5°. W. H. G.

Ketens. XIII. Action of Diphenylketen on Carbonyl Derivatives. Hermann Staudinger [and, in part, with J. Buchwitz] (*Ber.*, 1909, **42**, 4249—4262. Compare Abstr., 1908, i, 246, 318, 410, 411, 602).—Experiments have been made by heating diphenylketen in the form of its solid quinoline derivative with equivalent quantities of various ketones at 130° for 1·5 hours, and determining the velocity of reaction by the amount of carbon dioxide eliminated. The reaction proceeds in two stages: the first consisting in the formation of the β-lactone: $CR_2{:}O + CPh_2{:}CO \longrightarrow \begin{matrix} CR_2{-}O \\ | \quad | \\ CPh_2{\cdot}CO \end{matrix}$, and the second in the decomposition of the lactone into carbon dioxide and an olefine derivative: $\begin{matrix} CR_2{-}O \\ | \quad | \\ CPh_2{\cdot}CO \end{matrix} \longrightarrow CO_2 + CR_2{:}CPh_2$.

It is assumed that the second reaction proceeds with an infinitely greater velocity than the first. The following results have been obtained with the ketones, the formulæ of which are given: R′·CO·CH:CHPh, 82·3; R′·CO·CN, 76·3; R′·COH, 65·9; R′·COPh, 42·5; R′·COMe, 32·8; R′·COCl, 5·5; R′·CO·O·CO·CH:CHPh, 5·3; R′·CO·OEt, 5·4; R′·CO·NPh$_2$, 0·0; R″·CO·CH:CH·CH:CHPh, 85·7; R″·COPh, 55·6; R″·COMe, 20·7, where R′ = ·CH:CHPh, R″ = CH:CH·CH:CHPh, and the numbers give the percentage amount of the ketone which enters into the reaction. The influence of a double linking on the reactivity of the ketone is not marked, but the results indicate that the reactivity of a ketone with diphenylketen is least when an NR_2 or OR group is attached to the carbonyl, that is, carboxylic derivatives. The carbonyl group, on the other hand, is much more reactive when attached to H, Me, or Ph, and is most reactive when unsaturated groups, for example, cyano and cinnamenyl, are present. The results are probably explicable if the state of saturation of the carbonyl group is taken into account in the different compounds.

ββ-Diphenyl-α-styrylacrylonitrile, CHPh:CH·C(CN):CPh$_2$, obtained

from diphenylketen-quinoline and cinnamoylformonitrile, crystallises in golden-yellow plates, m. p. 157—159°. It is not hydrolysed when boiled with acids or alkalis, but reacts with a chloroform solution of bromine, yielding the *dibromide*, $C_{23}H_{17}NBr_2$, m. p. 143—144°.

Cinnamaldehyde and diphenylketen-quinoline yield *aaδ-triphenylbutadiene*, $CHPh{:}CH{\cdot}CH{:}CPh_2$, which crystallises in colourless needles, m. p. 101·5—102°. With bromine it yield a *bromo*-derivative, $C_{22}H_{17}Br$, in the form of colourless crystals, m. p. 146—148°.

Benzylideneacetophenone and diphenylketen-quinoline yield *aaβδ-tetraphenylbutadiene*, $CHPh{:}CH{\cdot}CPh{:}CPh_2$, and 3-*benzoyl*-1 : 1 : 2-*triphenyl*-4-cyclo*butanone*, $COPh{\cdot}CH<^{CHPh}_{CO}>CPh_2$, which can be separated by means of ether, in which the hydrocarbon is somewhat more readily soluble. The ketone crystallises in colourless plates, m. p. 190°. It does not combine with bromine, is stable towards oxidising agents, but reacts with alkalis, yielding diphenylacetic acid. Its *dioxime* has m. p. 191—192°. The tetraphenylbutadiene crystallises in colourless, compact prisms, m. p. 146—148°. It yields a *dibromide*, $C_{28}H_{22}Br_2$, in the form of yellow crystals, m. p. 144—145°, and when oxidised in acetone solution with potassium permanganate or dichromate, yields benzaldehyde and *triphenylacraldehyde*, $CPh_2{:}CPh{\cdot}CHO$, colourless needles, m. p. 175°.

Cinnamylideneacetophenone and diphenylketen-quinoline yield *aaβζ-tetraphenylhexa-*$\Delta^{\alpha\gamma\epsilon}$*-triene*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CPh{:}CPh_2$, and 3-*benzoyl*-1 : 1-*diphenyl*-2-*styryl*-4-cyclo*butanone*,

$$CHPh{:}CH{\cdot}CH<^{CH(COPh)}_{CPh_2}>CO.$$

The ketone crystallises in colourless needles, m. p. 120—122°, and reacts with bromine, yielding the *bromo*-derivative, $C_{31}H_{23}O_2Br$, m. p. 148—149°. The hexatriene crystallises in yellow prisms, m. p. 158—160°, and yields a *tetrabromide*, $C_{30}H_{24}Br_4$, m. p. 148—150°.

In the combination of the above compounds with bromine, one double linking always remains intact, and this is supposed to be the linking in the $>C{:}CPh_2$ group. Definite products could not be isolated by heating diphenylketen-quinoline with either benzylideneacetone or cinnamylideneacetone, nor yet with methyl cinnamate or cinnamodiphenylamide. J. J. S.

Phenylhydrazones of 2-Acetyl-1-naphthol [1-Hydroxy-β-naphthyl Methyl Ketone] : Alkali-insoluble Naphthols. Henry A. Torrey and C. M. Brewster (*J. Amer. Chem. Soc.*, 1909, 31, 1322—1325).—It has been shown by Torrey and Kipper (Abstr., 1908, i, 461) that the phenylhydrazones of certain hydroxyacetophenones are insoluble in aqueous alkali hydroxides, and it is stated that this insolubility is due to the combined influence of the side-chain containing the phenylhydrazine residue in the ortho-position to the hydroxyl group and of another group in the ring, such as the methoxy-group. In the present paper an account is given of the phenylhydrazones of 1-hydroxy-β-naphthyl methyl ketone and its bromo-derivative. These compounds are also insoluble in aqueous

alkali hydroxides, the insolubility in this case being due to the joint effect of the ·CMe:N·NHPh group in the ortho-position to the hydroxyl group and of the hydrocarbon residue, ·CH:CH·CH:CH·. The hydrazones are very stable, and can be boiled with aqueous alkali hydroxide without undergoing any change. The presence of a bromine atom in the naphthalene ring or in the phenyl group does not affect the insolubility.

4(?)-*Bromo*-1-*hydroxy*-β-*naphthyl methyl ketone*, $OH·C_{10}H_5Br·COMe$, m. p. 126—127°, obtained by the action of bromine on an alcoholic solution of the ketone, forms yellowish-green crystals, and condenses with benzaldehyde with production of the *benzylidene* derivative, $OH·C_{10}H_5Br·CO·CH:CHPh$, m. p. 176—177°, which forms orange-red crystals. The *phenylhydrazone*, $OH·C_{10}H_6·CMe:N·NHPh$, m. p. 136—137°, forms white needles. The p-*bromophenylhydrazone*, m. p. 185—186°, forms silvery-white plates, and the m-*nitrophenylhydrazone*, m. p. 232—233° (decomp.), deep red, compact needles.

The *phenylhydrazone* of the bromo-derivative crystallises in pale yellow needles, and decomposes at 159°. The p-*bromophenylhydrazone*, m. p. 160° (decomp.), forms colourless crystals, and the m-*nitrophenylhydrazone*, m. p. 201—204° (decomp.), deep, orange crystals.

E. G.

Two Isomeric *cyclo*Hexane β-Diketones. Georges Leser (*Compt. rend.*, 1909, 149, 1080—1081).—When ethyl acetate is condensed with 1 : 1-dimethyl-3-*cyclo*hexanone (Abstr., 1899, i, 743), 4-*acetyl*-1 : 1-*dimethyl*-3-cyclo*hexanone*, b. p. 111—112°/13 mm., m. p. 28—29°, is formed. It yields a *semicarbazone*, m. p. 171°, has all the properties of a β-diketone, and does not react with magnesium methyl iodide.

The isomeric substance, 2-acetyl-1 : 1-dimethyl-3-*cyclo*hexanone (*loc. cit.*), is soluble in alkalis, does not form a copper derivative, and reacts with magnesium methyl iodide, forming 2-*acetyl*-1 : 1 : 3-*trimethyl*cyclo*hexan*-3-*ol*, $CH_2<\begin{matrix}CH_2\text{———}CH_2\\CMe(OH)·CHAc\end{matrix}>CMe_2$, m. p. 88—89°, b. p. 232°/750 mm., which crystallises in prismatic needles. On boiling with 20% sulphuric acid, it furnishes the corresponding *dimethyltetrahydroacetophenone*, b. p. 207—208°/745 mm., D^{15} 0·935, n_D 1·4776, which has a strong odour of peppermint. On oxidation with permanganate, this furnishes an acid, $C_8H_{14}O_4$, m. p. 86°. T. A. H.

Quinhydrones from Chloranil and Aromatic Hydrocarbons. Hermann Haakh (*Ber.*, 1909, 42, 4594—4596. Compare Schlenk, Abstr., 1909, i, 807).—Tetrachloro-*p*-benzoquinone forms intensely-coloured *quinhydrones* with stilbene and naphthalene, which are stable at about 100°, but dissociate into their components at the ordinary temperature; the violet *quinhydrones* derived from acenaphthene and acenaphthylene are stable at the ordinary temperature. Interesting is the fact that solutions of chloranil in benzene and xylene are faintly orange and yellowish-red respectively, indicating in the second case partial quinhydrone formation. W. H. G.

Preparation of Halogenated Anthraquinones. Badische Anilin- & Soda-Fabrik (D.R.-P. 214714).—Halogenated anthraquinonesulphonic acids were formerly obtained by treating the anthraquinonesulphonic acids in concentrated or fuming sulphuric acid with halogen or halogenating substances. It has now been found that in these acids the sulphonic group is replaced by halogen when this reaction occurs in the presence of water.

A *trichloroanthraquinone* (probably 1 : 3 : 4-) is obtained by the action of potassium chlorate and hydrochloric acid on an aqueous solution of sodium 1 : 4-dichloroanthraquinone-β-sulphonate. It forms yellow needles, m. p. 237°.

1 : 4-Dichloroanthraquinone-α-sulphonic acid gives a *trichloroanthraquinone*, melting at 253—254°. A *dichlorobromoanthraquinone*, m. p. 233°, is produced by the action of bromine and water at 190° on sodium 1 : 4-dichloroanthraquinone-β-sulphonate. F. M. G. M.

Preparation of Halogenated Nitroanthraquinones. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 214150).—The nitroanthraquinonesulphonic acids, like the anthraquinonesulphonic acids, yield halogenated derivatives when treated with aqueous chlorine, the sulphonic group being eliminated in each case.

1-*Chloro*-5-*nitroanthraquinone* is prepared from sodium 1 : 5-nitroanthraquinonesulphonate by treatment with sodium chlorate and hydrochloric acid; it forms pale yellow needles. 1 : 6-, 1 : 7-, and 1 : 8-*Chloronitroanthraquinones* were similarly obtained, and the colours of their solutions in various solvents are tabulated in the patent.

F. M. G. M.

[Preparation of Thioglycine Derivatives of Anthraquinone.] Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 213960. Compare Abstr., 1909, i, 496, 941).—The action of the previously-described thiolanthraquinones on chloroacetylaminoanthraquinones leads to the formation of anthraquinonethioglycines having the general formula (A = anthraquinone) $A{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}A$.

The following components and their condensation products are described in the patents:

Chloroacetyl-1-*aminoanthraquinone*, greenish-yellow needles, and its condensation *products* with α- and β-thiolanthraquinones.

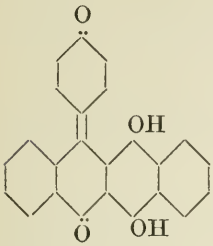
Chloroacetyl-1-*amino*-4-*hydroxyanthraquinone*, orange-red needles, and the *products* of its condensation with α-thiolanthraquinone and with 1 : 5-dithiolanthraquinone.

Chloroacetyl-1 : 4-*diaminoanthraquinone*, yellowish-brown prisms, and its *compound* with α-thiolanthraquinone.

Chloroacetyl-1 : 5-*diamino*-4 : 8-*dihydroxyanthraquinone*, and its condensation *product* with α-thiolanthraquinone. F. M. G. M.

The Naphthacene Series. III. Hugo Voswinckel and Fritz de Weerth (*Ber.*, 1909, **42**, 4648—4650. Compare Abstr., 1906, i, 99; 1909, i, 166).—When naphthacenediquinone, acetic acid, and an excess

of sulphuric acid are heated to a higher temperature than is required for the preparation of 6 : 11-dihydroxy-6-acetoxy-11-*p*-hydroxyphenyldihydronaphthacenequinone, the chief product is 5 : 12-*dihydroxy*-11-*phenonaphthacenequinone* (annexed formula), which crystallises in dark red, pointed prisms, soluble in dilute sodium hydroxide or in concentrated sulphuric acid to red solutions. The diacetyl derivative, $C_{24}H_{12}O_4Ac_2$, has m. p. 264°. The same quinone is formed when the primary condensation product (dihydroxyacetoxy-hydroxyphenyldihydronaphthacenequinone) is heated with acetic and sulphuric acids; the reduction then proceeds at the expense of part of the quinone, and the product $C_{24}H_{16}O_5$, m. p. 174° (Abstr., 1909, i, 167) is also obtained.



5 : 12-*Dihydroxy*-6-*keto*-11-*hydroxyphenyl*-6 : 11-*dihydronaphthacene*,

$$C_6H_4<\begin{matrix}CH(C_6H_4\cdot OH)\cdot C\cdot C(OH)\\ CO\text{———}C\cdot C(OH)\end{matrix}>C_6H_4,$$

obtained by reducing the phenodihydroxynaphthacenequinone with an alkaline solution of sodium hyposulphite, separates as an orange-coloured, crystalline powder, m. p. 225°. The *triacetate*, $C_{24}H_{13}O_4Ac_3$, forms a pale yellow, crystalline powder, m. p. 206—210°. When the quinone is reduced with zinc dust and glacial acetic acid, a *product*, $C_{24}H_{16}O_3$, is obtained as a pale yellow, crystalline powder with no definite m. p. Its *acetyl* derivative, $C_{26}H_{18}O_4$, has m. p. 171°.

J. J. S.

Stereo- and Structural Isomerides obtained by the Introduction of Acyl Radicles into β-Hydroxylamines. I. Guido Cusmano (*Gazzetta*, 1909, 39, ii, 336—346).—The author describes observations on the action of acyl chlorides on β-hydroxylamines, and shows that this reaction affords a means of obtaining substituted hydroxy-iminic acids.

The compound described by Beckmann and Pleissner (Abstr., 1891, 936) as pulegonehydroxylamine benzoate, m. p. 137—138°, which may be prepared by the action of benzoyl chloride on pulegonehydroxylamine in ether, is, in reality, anti-*menthonylbenzhydroximic acid*, $\begin{matrix}Ph\cdot C\cdot O\cdot C_{10}H_{17}O\\ OH\cdot N\end{matrix}$, $[\alpha]_D^{20}$ −20·14° (in alcohol); in freezing acetic acid it has the normal molecular weight, and when treated with sodium ethoxide, it yields sodium benzhydroxamate and pulegone.

syn-*Menthonylbenzhydroximic acid*, $\begin{matrix}Ph\cdot C\cdot O\cdot C_{10}H_{17}O\\ N\cdot OH\end{matrix}$, prepared by the action of concentrated hydrochloric acid on the *anti*-compound, or by varying the conditions under which benzoyl chloride and pulegonehydroxylamine react, has m. p. 182°, $[\alpha]_D^{22}$ −42·44° (in methyl alcohol), and exhibits normal cryoscopic behaviour in acetic acid. Its *hydrochloride*, m. p. 58° (decomp.), is converted at 100° into an oil, which, with sodium carbonate, yields benzhydroxamic and benzoic

acids and a *substance*, m. p. 84°, soluble in hydrochloric acid with formation of *syn*-menthonylbenzhydroximic acid.

The *menthonyl ether* of *benzhydroxamic acid*, $\begin{matrix}Ph\cdot C\cdot OH\\ \|\\ N\cdot OC_{10}H_{17}O'\end{matrix}$ obtained, together with *syn*-menthonylbenzhydroximic acid, by the action of gaseous hydrogen chloride on the *anti*-acid suspended in ether, forms plates, m. p. 96°, and may be converted into *syn*-menthonylbenzhydroximic acid by the action of hydrochloric acid.

T. H. P.

Syntheses in the Camphor and Terpene Series. II. Complete Synthesis of Camphoric Acid and Camphor. Gustav Komppa (*Annalen*, 1909, **370**, 209—233. Compare Abstr., 1909, i, 726).—The present communication contains a detailed account of the synthesis of camphoric acid from *apo*camphoric acid, thereby establishing the validity of Bredt's camphor formula.

When diketo*apo*camphoric acid (1 mol.) is treated with methyl iodide (2 mols.) and sodium methoxide (2 mols.) in methyl-alcoholic solution, it yields a mixture of methyl diketocamphorate and methyl-ketomethoxydehydrocamphorate, which is resolved by treatment with an aqueous solution of sodium carbonate, in which the first named is soluble. *Methyl diketocamphorate*, $\begin{matrix}CO\cdot CMe(CO_2Me)\\ |\\ CO—CH(CO_2Me)\end{matrix}>CMe_2$, crystallises in stout plates, m. p. 85—88°; the *copper* salt, $C_{24}H_{30}O_{12}Cu$, crystallises in stellate groups of bluish-green prisms; the acid is reduced in aqueous solution by sodium amalgam, yielding 4 : 5-*dihydroxycamphoric acid*, obtained as a viscid, yellow syrup; the *silver*, $C_{10}H_{14}O_6Ag$, and *barium* ($1H_2O$) salts are amorphous, white powders.

2 : 2 : 3-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid*, $\begin{matrix}CH_2\cdot CMe(CO_2H)\\ |\\ CH=\!=C(CO_2H)\end{matrix}>CMe_2$, is obtained by reducing 4 : 5-dihydroxycamphoric acid with hydriodic acid and red phosphorus, also by hydrolysing the ester resulting from the action of diethylaniline on ethyl α-bromocamphorate; it crystallises in small, colourless, monoclinic prisms, m. p. 221—223°, and is converted by a solution of hydrogen bromide in glacial acetic acid at 120—125° under pressure into *β-bromocamphoric acid*, obtained as an oil, which, when acted on by zinc dust and glacial acetic acid, yields a mixture of camphoric and *iso*camphoric acids. The *semi-anilide* of *r*-camphoric acid, $C_{16}H_{21}O_3N$, prepared by the action of aniline on *r*-camphoric acid in alcoholic solution, crystallises in small, rhombohedra or long needles, m. p. 214·5°—215·5° (corr.).

Methyl 4-*keto*-5-*methoxydehydrocamphorate*, $\begin{matrix}C(OMe):C(CO_2Me)\\ |\\ CO—CMe(CO_2Me)\end{matrix}>CMe_2$, is an ether-like oil, b. p. 156—157°/8 mm., $D_{17\cdot5}^{17\cdot5}$ 1·188, n_D 1·49212, which, when reduced with sodium amalgam and methyl alcohol, yields the corresponding hydroxy-acid, from which dehydrocamphoric acid is obtained by treatment with hydriodic acid and red phosphorus.

W. H. G.

Condensation Products from Camphor. Marcel Guerbet (*Compt. rend.*, 1909, **149**, 931—933.* Compare Abstr., 1909, i, 310).—The formation of neutral, oily products when the mixture resulting from the action of sodium on a solution of camphor in toluene is heated at 280° has been observed by Montgolfier (Abstr., 1878, 891), who supposed them to have the composition $(C_{10}H_{10})_n$. The oil has now been distilled, and from the fraction b. p. 326—335° two condensation products isolated.

(i) *Bornylenecamphor*, $C_8H_{14}<\begin{matrix}C=C-\\ CO\ CH_2\end{matrix}>C_8H_{14}$ occurs as colourless needles, m. p. 93°, $[\alpha]_D$ +69·2° in alcohol. It unites with hydrogen bromide, forming a *compound*, $C_{20}H_{31}OBr$, m. p. 202—203°. Bromine attacks it, liberating hydrogen bromide and yielding *bromobornylenecamphor*, $C_{20}H_{29}OBr$, m. p. 101°. Warm fuming nitric acid converts bornylenecamphor into a *nitro*-derivative, $C_{20}H_{30}O{\cdot}NO_2$, which crystallises in colourless, rhombic tablets, m. p. 204°, and forms a *sodium* salt, $C_{20}H_{28}ONa{\cdot}NO_2,3H_2O$, occurring as pearly leaflets.

(ii) *Bornylcamphor*, $C_8H_{14}<\begin{matrix}CH{\cdot}CH\\ CO\ CH_2\end{matrix}>C_8H_{14}$, crystallises in needles, m. p. 77·5°, and can also be prepared by the reduction of benzylidenecamphor by sodium amalgam in acid alcoholic solution.

W. O. W.

Composition of Oil of Turpentine. Eugène Darmois (*Compt. rend*, 1909, **149**, 730—733. Compare Abstr., 1908, ii, 747).—A further application of measurements of rotatory dispersion to the determination of the composition of optically active hydrocarbons. Dextrorotatory turpentine contains *d*-pinene, together with a hydrocarbon showing feebly lævorotatory dispersive power and having $[\alpha]_D$ −21·7°. The latter appears also to be present in French lævo-oils, and may be identical with nopinene. The b. p. of the oil from *Pinus halepensis* remains constant at 155° for 90% of the product; the distillate shows strong dispersion, and has $[\alpha]_D$ +82·8°, m. p. −50°.

By the application of Biot's law of mixtures as previously indicated, the proportion of pinene in French lævo-oils and in Algerian dextro-oils is found to be 62%. W. O. W.

Hydrogenation in the Terpene Series. G. Vavon (*Compt. rend.*, 1909, **149**, 997—999).—Pinene rapidly absorbs hydrogen in presence of platinum-black. In this way the α-pinene (Algerian) prepared by Darmois (preceding abstract) has furnished, in quantitative yield, a *hydrocarbon*, $C_{10}H_{18}$, b. p. 166°/755 mm., $[\alpha]_D$ +22·7°, D_{15}^{15} 0·861, solidifying at about −45°. It differs from the hydrocarbon described by Sabatier and Senderens (Abstr., 1901, i, 459) in remaining unaltered on exposure to air. Under the same conditions, French *l*-pinene yields the same compound, but having $[\alpha]_D$ −21·3°; α- and β-pinene therefore appear to yield the same substance on hydrogenation.

Camphene forms a *hydrocarbon*, $C_{10}H_{18}$, m. p. about 87°, which is not identical with that obtained by Sabatier and Senderens (*loc. cit.*)

* and *J. Pharm. Chim.*, 1910, [vii], **1**, 5—10.

by the action of water on the magnesium derivative of camphene hydrochloride.

Limonene, $[\alpha]_D$ + 121·3°, combines with 4H, giving an inactive *hydrocarbon*, b. p. 169°, D_{15}^{15} 0·803. Maleic, fumaric, cinnamic, and erucic acids have been hydrogenated in the same way. W. O. W.

[α-Terpinene.] Karl Auwers. (*Ber.*, 1909, **42**, 4427—4429. Compare Abstr., 1909, i, 592).—Polemical. A reply to Semmler (Abstr., 1909, i, 942). R. V. S.

Constituents of Ethereal Oils. I. Terpinolene. II. Terpinene. Friedrich W. Semmler and Endre Schossberger (*Ber.*, 1909, **42**, 4644—4647).—I. Pure terpinolene is best prepared by the action of zinc dust on an ethereal-alcoholic solution of the pure tetrabromide, m. p. 115—116°. When acetic acid is used, the product always contains appreciable amounts of terpinene. Pure terpinolene has b. p. 67—68°/10 mm., D^{20} 0·854, and n_D 1·484.

II. Terpinene. Polemical (compare Auwers, preceding abstract). J. J. S.

Cryptomeria Japonica Oil. H. Kimura (*Ber. Deut. pharm. Ges.*, 1909, **19**, 369—387).—The oil distilled from the wood of this tree is shown to consist to the extent of 60% of the sesquiterpenes, *l*-cadinene and suginene, the residue being a sesquiterpene alcohol, cryptomeriol (compare Kimoto, *Chem. Centr.*, 1902, ii, 382; Keimatsu, *Pharm. J.*, 1905, 189).

On steam distillation the wood yields 1·5% of a yellow oil, which darkens and thickens on standing. The re-distilled oil has D 0·9590, $[\alpha]_D$ − 22°32′, contains no methoxyl, nitrogen, sulphur, or halogens, and is free from acids, aldehydes, and phenols.

The terpene portion was separated by treating the original oil with metallic sodium or potassium. It consisted of a mixture of sesquiterpenes, which was resolved into its components by treatment with hydrogen chloride, which furnished a solid and a liquid dihydrochloride. The former had m. p. 117—118° and $[\alpha]_D$ − 37°4′ in chloroform, and proved to be identical with *l*-cadinene dihydrochloride from cade oil. The liquid hydrochloride on treatment with sodium acetate and acetic acid regenerated a new sesquiterpene, *suginene*, D 0·918, $[\alpha]_D$ − 10°34′, which yields a liquid *dihydrobromide*, b. p. 140—150°/16 mm., D 0·988, $[\alpha]_D$ − 11°15′. The sesquiterpene regenerated from this had D 0·921 and $[\alpha]_D$ + 14°43′, whilst that regenerated from the liquid *dihydriodide* had D 0·911 and $[\alpha]_D$ − 24°21′. No crystalline derivatives of suginene could be obtained, but it appears to be oxidised to an alcohol by treatment with bromine water.

The alcoholic portion of the oil was isolated by treatment with potassium wire, the sesquiterpene portion being then removed by distillation under reduced pressure. The potassium derivative was freed from excess of potassium and other impurities by solution in ether. The potassium derivative, on treatment with water, furnished *cryptomeriol*, $C_{15}H_{25}{\cdot}OH$, b. p. 162—163°/10 mm., D 0·964,

$[\alpha]_D$ −37°5′, a thick, colourless oil. The potassium derivative of this, when treated with carbon disulphide, yielded a *xanthic* ester,

$$C_{15}H_{25}O\cdot CS\cdot SK,$$

which on addition of water did not regenerate the original alcohol, but colourless, crystalline iso*cryptomeriol*, $C_{15}H_{26}O$, m. p. 135—136°, and a new liquid *alcohol*, $[\alpha]_D$ −3°25′. On treatment with formic acid, cryptomeriol yielded a *sesquiterpene*, D 0·918, b. p. 143—144°/13 mm., $[\alpha]_D$ −1°5′, and with phosphoric oxide, a second *sesquiterpene*, D 0·917, $[\alpha]_D$ +56°26′, which was also prepared from the first sesquiterpene by the action of phosphoric oxide. Both gave liquid products with gaseous halogen acids.

Cadinene cannot be regenerated unchanged from its compounds with the halogen acids. T. A. H.

Volatile Oil of Rhus Cotinus ("Young Fustic"). Gustave Perrier and A. Fouchet (*Bull. Soc. chim.*, 1909, [iv], 5, 1074—1075).—The leaves and twigs on steam distillation yield 0·1% of a colourless, volatile oil with an odour somewhat recalling that of oil of turpentine. The oil has D^{15} 0·875, n_D 1·4693, $[\alpha]_D$ +13°, is completely soluble in alcohol of 94°, is acid to litmus, contains free alcohols, and gives the aldehyde reaction with Schiff's reagent. T. A. H.

Catalytic Oxidation of Guaiacum Resin by Copper. Hector A. Colwell (*J. Physiol.*, 1909, 39, 358—360).—Both metallic copper and its salts have a catalytic oxidising action on guaiacum, which is remarkable among the other metals examined for its intensity. W. D. H.

Preparation of Indican. Henri ter Meulen (*Rec. trav. chim.*, 1909, 28, 339—341).—In a previous paper (Abstr., 1900, i, 404) the author has shown with Hoogewerff, that indican may be prepared conveniently from plants containing it, by extraction with boiling water, but Perkin and Bloxam have stated recently (Trans., 1907, 91, 1715) that in their experience extraction with water gives a smaller yield of indican than is obtained with acetone as a solvent.

The author has repeated the previous work with material supplied to him by Perkin and Bloxam, and finds that, using his modified process (*Rec. trav. chim.*, 1905, 24, 468), he obtains 2·7% of indican as compared with 3·166% found by Perkin and Bloxam, so that extraction with hot water does not necessarily involve any material loss of glucoside. T. A. H.

Active Principle of a Benin Spear Poison. Patrick P. Laidlaw (*J. Physiol.*, 1909, 39, 354—357).—The supply of poison was obtained from two spear heads from Benin. Although attempts to prepare a pure crystalline toxic substance failed, owing to impurities, there is no doubt that the poison is a glucoside which has the solubilities and physiological properties of strophanthin; it also gives the characteristic colour reaction of that substance. W. D. H.

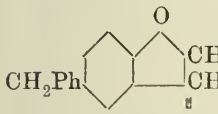
Discovery of the Optical Activity of Tannin. Edmund O. von Lippmann (*Ber.*, 1909, **42**, 4678—4679. Compare Rosenheim, Abstr., 1909, i, 599).—C. Scheibler (*Zeitsch. Zuckerind.*, 1866, **16**, 33) appears to have been the first to draw attention to the optical activity shown by certain specimens of tannin. J. J. S.

Furfurylpropylcarbinol. Mlle. Eugènie Jolkver (*Rec. trav. chim.*, 1909, **28**, 439—443).—*Furfurylpropylcarbinol*,

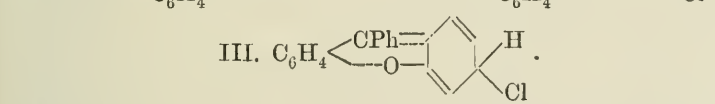
$$C_4OH_3\cdot CHPr^{\alpha}\cdot OH,$$

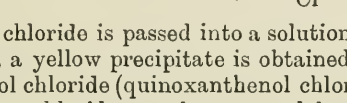
b. p. 92—93°/12 mm. or 195—198°/760 mm., prepared by Grignard's method (Abstr., 1901, i, 680) from magnesium propyl bromide and furfuraldehyde, is a colourless liquid, which becomes yellow on exposure to light. The corresponding *chloride* has b. p. 90—91°/6 mm. or 94—95°/10 mm., and the *acetate*, b. p. 96—97°/22 mm. or 106°/28 mm., is a colourless, mobile liquid of pleasant odour. T. A. H.

4-Benzylcumaran. Charles Marschalk (*Ber.*, 1909, **42**, 4485—4487). — 4-*Benzylcumaran* (annexed formula), prepared by the reduction of 4-benzoylcumaran (compare Abstr., 1907, i, 950) by means of sodium and alcohol, forms white crystals, m. p. 61°, and dissolves in concentrated sulphuric acid, giving a yellow solution, which becomes green on addition of ferric chloride. This compound is presumably the mother substance of the catechin group. T. H. P.



Triphenylmethyl. XVIII. Quinocarbonium Salts. Moses Gomberg and Lee H. Cone (*Annalen*, 1909, **370**, 142—208. Compare Abstr., 1907, i, 504; 1909, i, 144).—A complete parallelism is shown to exist between the salts of triphenylcarbinol and its derivatives and the salts of xanthenol and analogous substances, from which the conclusion is drawn that the compounds which have been regarded previously as carboxonium salts (compare Kehrmann, Abstr., 1900, i, 61; Werner, Abstr., 1902, i, 50) are really carbonium salts, and, like triphenylcarbinol chloride, capable of existing in a benzenoid (I) and a quinonoid (II and III) form:

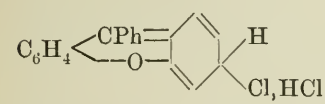




When hydrogen chloride is passed into a solution of xanthenol in an indifferent solvent, a yellow precipitate is obtained, which is a hydrochloride of xanthenol chloride (quinoxanthenol chloride hydrochloride); the mol. of hydrogen chloride may be removed by suitable treatment, leaving a colourless chloride. The normal, colourless xanthenol chlorides are very similar in their chemical behaviour to triphenylcarbinol chloride. They give yellow solutions when dissolved in liquid sulphur dioxide, showing that they exist in two tautomeric

forms, a further proof of which is shown by the behaviour of phenyl-*p*-bromoxanthenol bromide, which when treated with silver chloride yields phenyl-*p*-chloroxanthenol chloride.

The formation of coloured derivatives is induced, not only by sulphur dioxide and hydrogen chloride, but also by metallic halides, sulphuric acid, and perchloric acid. The last-mentioned acid forms stable, crystalline salts, not only with xanthenol derivatives, but also with those of triphenylmethane, which latter do not contain oxygen. The colour of these salts cannot be due, therefore, to the formation of oxonium salts.



Phenylxanthenol (compare Bünzly and Decker, Abstr., 1904, i, 912) when treated in chloroform with a solution of acetyl chloride and subsequently with hydrogen chloride yields *phenylquinoxanthenol chloride hydrochloride* (annexed formula), crystallising in glistening, reddish-orange prisms; the *chloride*, $O{:}(C_6H_4)_2{:}CPhCl$, is obtained by passing air through a solution of the hydrochloride just described at about 50—60° in the complete absence of water; it crystallises in colourless prisms, m. p. 105—106°. A solution of the chloride in benzene (1) when heated under pressure with silver yields an *unsaturated* compound, which, in analogy to triphenylmethyl, absorbs oxygen quite readily, yielding *phenylxanthenol peroxide*, $\left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CPh\right]_2O_2$, transparent, colourless, glistening leaflets, m. p. 219° (decomp.), and (2) when treated with magnesium benzyl chloride yields *αβ-diphenyl-α-xanthylethane*, $O{:}(C_6H_4)_2{:}CPh{\cdot}CH_2Ph$, colourless, rhombic prisms, m. p. 169°. The following additive compounds of the chloride have been prepared: *ferrichloride*, $C_{19}H_{13}OCl,FeCl_3$, brownish-red spangles, sinters at 167°, m. p. 170°; *mercurichloride*,

$$C_{19}H_{13}OCl,HgCl_2,$$

white powder, sinters at 230°, m. p. 248—250° (decomp.); *perbromide*, $C_{19}H_{13}OCl,Br_2$, unstable, orange-yellow powder, sinters at 146°, m. p. 150° (decomp.); *periodide*, $C_{19}H_{13}OCl,I_2$, brownish-red, crystalline powder; *perchloride*, $C_{19}H_{13}OCl,Cl_2$, orange-red needles. *Phenylxanthenol hydrogen sulphate*, $C_{19}H_{13}O{\cdot}SO_4H$, forms stellate aggregates of orange crystals, m. p. 175°; the *perchlorate*, $C_{19}H_{13}O{\cdot}ClO_4$, obtained by the action of silver perchlorate on the chloride or directly from perchloric acid and phenylxanthenol, crystallises in golden, transparent prisms, m. p. 281—282°.

The following compounds are obtained by methods similar to those just described.

p-*Tolylxanthenol*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C<\begin{matrix}C_6H_4Me\\OH\end{matrix}$, prepared from xanthone and *p*-iodotoluene, crystallises in groups of small, transparent plates, m. p. 150°. p-*Tolylquinoxanthenol chloride hydrochloride*,

$$O<\begin{matrix}C_6H_4\\C_6H_4(Cl,HCl)\end{matrix}>C{\cdot}C_7H_7,$$

is an unstable, brown, crystalline substance. The *chloride*,

$$O{:}(C_6H_4)_2{:}C(C_7H_7)Cl,$$

crystallises in colourless prisms, m. p. 131°; *ferrichloride*,

$$C_{20}H_{15}OCl,FeCl_3,$$

yellowish-brown crystals, sinters at 205°, m. p. 211°; *zinc chloride*, $C_{20}H_{15}OCl,ZnCl_2$, brownish-yellow needles, sinters at 233°, m. p. 240—247° (decomp.); *perbromide*, $C_{20}H_{15}OCl,Br_2$, amorphous, brownish yellow powder; the *perchlorate*, $C_{20}H_{15}O\cdot ClO_4$, crystallises in yellow needles, m. p. 239°. p-*Tolylxanthenol peroxide*, $C_{40}H_{30}O_4$, forms colourless, glistening prisms, m. p. 212° (decomp.).

Phenyldinaphthoxanthenol, $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CPh\cdot OH$, prepared by oxidising benzylidene-β-dinaphthyl oxide in glacial acetic acid with lead peroxide, has m. p. 265—268°. *Phenyldinaphthoquinoxanthenol chloride hydrochloride*, $C_{27}H_{18}OCl_2$, crystallises in long, dark red, glistening needles, loses hydrogen chloride when heated, becomes white at 230°, m. p. 270—274°. *Phenyldinaphthoxanthenol chloride*, $C_{27}H_{17}OCl$, forms almost colourless crystals, m. p. 274°; the *ferrichloride*, $C_{27}H_{17}OCl,FeCl_3$, dark red needles; *stannichloride*, $C_{27}H_{17}OCl,SnCl_4$, red crystals, and *zinc chloride*, $C_{27}H_{17}OCl,ZnCl_2$, glistening, red needles, were analysed; the *hydrogen sulphate*, $C_{27}H_{17}O\cdot SO_4H,\frac{1}{2}H_2SO_4$, forms long, red needles, m. p. 145—150°; the *perchlorate*, $C_{27}H_{17}O\cdot ClO_4$, crystallises in scarlet leaflets with a golden shimmer, and does not melt at 280°.

p-*Methoxyphenyldinaphthoquinoxanthenol chloride hydrochloride*,

$$C_{28}H_{19}O_2Cl,HCl,$$

forms dark red, glistening crystals, m. p. 235° (decomp.). p-*Methoxyphenyldinaphthoxanthenol chloride*, $O:(C_6H_4)_2:C(C_6H_4\cdot OMe)Cl$, forms white crystals; the red, crystalline *additive* products with ferric chloride, m. p. 235—237°, stannic chloride, zinc chloride, and iodine were analysed; the *hydrogen sulphate*, $C_{28}H_{19}O_2\cdot SO_4H,\frac{1}{2}H_2SO_4$, bright red needles, m. p. 145°, and *perchlorate*, $C_{28}H_{19}O_2\cdot ClO_4$, were analysed.

p-*Chlorophenylxanthenol*, $O:(C_6H_4)_2:C(C_6H_4Cl)\cdot OH$, has m. p. 173°; the *chloride*, $C_{19}H_{12}OCl_2$, forms colourless, transparent prisms, m. p. about 104—105°, and when treated with alcohol yields p-*chlorophenylxanthenol ethyl ether*, $C_{21}H_{17}O_2Cl$, crystallising in tufts of colourless crystals, m. p. 120—121°; the *additive* compounds of the chloride with ferric chloride, m. p. 209—210°, zinc chloride, and bromine, m. p. 166° (decomp.), were analysed; they are orange-red, crystalline powders. p-*Chlorophenylxanthenol peroxide*, $C_{38}H_{24}O_4Cl_2$, prepared by the action of silver and air on a solution of the chloride in benzene, crystallises with benzene in colourless, glistening prisms, m. p. 213° (decomp.). p-*Chlorophenylquinoxanthenol chloride hydrochloride*,

$$C_{19}H_{12}OCl_2,HCl,$$

forms brownish-yellow needles.

p-*Bromophenylxanthenol*, $C_{19}H_{13}O_2Br$, crystallises in long, colourless, pointed needles, m. p. 183°; the *chloride*, $C_{19}H_{12}OBrCl$, forms transparent, colourless prisms, m. p. 118—119°; the *perchlorate*,

$$C_{19}H_{12}OBr\cdot ClO_4,$$

is a crystalline, orange powder, sinters at 295°, m. p. about 310° p-*Bromophenylquinoxanthenol chloride hydrochloride*, $C_{19}H_{12}OClBr,HCl$, crystallises in yellow needles. p-*Bromophenylxanthenol peroxide*,

$$C_{38}H_{24}O_4Br_2,$$

crystallises in colourless, rhombic plates, m. p. 210—211° (decomp.).

Phenyl-p-*chloroxanthenol*, $O<\begin{matrix}C_6H_3Cl\\C_6H_4\end{matrix}>CPh\cdot OH$, prepared from

4-chloroxanthone and magnesium phenyl bromide, crystallises in slender leaflets, m. p. 164°; the *chloride*, $C_{19}H_{12}OCl_2$, crystallises in rosettes of colourless rods, m. p. 151°. 4-*Chloroxanthone* was prepared as follows: 2 : 4-dichloroaniline is converted into 2 : 4-dichlorobenzonitrile, colourless prisms, m. p. 61°, which when hydrolysed yields 2 : 4-dichlorobenzoic acid, m. p. 164°; the latter substance when treated with sodium phenoxide and copper powder yields 4-chloro-2-phenoxybenzoic acid, m. p. 171°, which is converted by warm concentrated sulphuric acid into 4-chloroxanthone, m. p. 130°. The compound, m. p. 171°, described by Ullmann and Wagner is probably an isomeride (compare Abstr., 1907, i, 846). *Phenyl-p-chloroquinoxanthenol chloride hydrochloride*, $C_{19}H_{12}OCl_2,HCl$, is an extremely unstable, red, crystalline substance.

Phenyl-p-bromoxanthenol, $C_{19}H_{13}O_2Br$, prepared by way of 4-*bromo-2-phenoxybenzoic acid*, $C_{13}H_9O_3Br$, crystallising in rosettes of needles, m. p. 178°, and 4-*bromoxanthone*, colourless needles, m. p. 126°, is obtained in colourless crystals, m. p. 145°; the *bromide*, $C_{19}H_{12}OBr_2$, crystallises in almost colourless needles, m. p. 155°. *Phenyl-p-bromoquinoxanthenol bromide hydrobromide*, $C_{19}H_{12}OBr_2,HBr$, crystallises in orange-red prisms with a blue reflex.

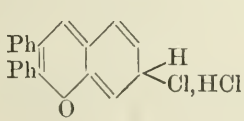
II. *Hydrochlorides and Perchlorates in the Triphenylmethane Series.*—Phenyldi-*p*-anisylcarbinol chloride combines with hydrogen chloride, forming a *hydrochloride*, $OMe\cdot C_6H_4\cdot CPh{:}C_6H_4(OMe)Cl,HCl$, obtained as a dark red oil. *Tri-p-anisylcarbinolchloride hydrochloride*,

$$C(C_6H_4\cdot OMe)_2{:}C_6H_4(OMe)Cl,HCl,$$

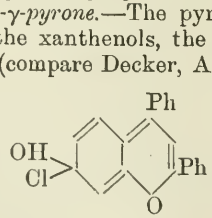
crystallises in dark red needles with a blue reflex (compare Baeyer and Villiger, Abstr., 1903, i, 811).

The *perchlorates* of the following compounds have been prepared and analysed: triphenylcarbinol, $C_{19}H_{15}\cdot ClO_4$, red crystals, m. p. 150°; diphenyl-*p*-tolylcarbinol, $C_{20}H_{17}\cdot ClO_4$, brown crystals; tri-*p*-tolylcarbinol, $C_{22}H_{21}\cdot ClO_4,\frac{1}{2}C_6H_5\cdot NO_2$, glistening, violet crystals, m. p. 187°; *p*-chlorotriphenylcarbinol, $C_{19}H_{14}Cl\cdot ClO_4$, compact, red crystals, m. p. 142—144°; *p*-bromotriphenylcarbinol, red crystals with a blue reflex, m. p. 151°; tri-*p*-chlorotriphenylcarbinol, small, brownish-red plates with a violet reflex, m. p. 172—174°; tri-*p*-bromotriphenylcarbinol, $C_{19}H_{12}Br_3\cdot ClO_4$, dark brownish-red crystals, m. p. 174—175°; diphenyl-*p*-anisylcarbinol, $C_{20}H_{17}O\cdot ClO_4$, red needles, m. p. 192°; phenyldi-*p*-anisylcarbinol, dark red needles, m. p. 112—113°; tri-*p*-anisylcarbinol, $C_{22}H_{21}O_3\cdot ClO_4$, dark purple needles, m. p. 195°.

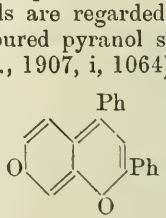
III. *Derivatives of Benzo-γ-pyrone.*—The pyranols are regarded as being strictly analogous to the xanthenols, the coloured pyranol salts being quinocarbonium salts (compare Decker, Abstr., 1907, i, 1064).



(I.)



(II.)



(III.)

2 : 3-*Diphenylbenzopyranol chloride hydrochloride* (formula I) crystallises in long, yellow needles.

[With O. B. Winter.]—*7-Hydroxy-2 : 4-diphenylbenzopyranol chloride hydrochloride*, $C_{21}H_{16}O_2Cl_2$, forms orange-red crystals; it loses 1HCl when dry air is passed through the solution in chloroform, yielding the orange-yellow quinonoid *chloride* (formula II); if the solution be heated, another mol. of hydrogen chloride is evolved, with the formation of the *quinone* (formula III), an amorphous, red powder.

IV. *Acridine Derivatives.*—The salts of the phenylacridols are probably quinocarbonium salts of the same type as the coloured salts of phenylxanthenol.

5 : 10-*Diphenylacridol chloride hydrochloride*,

$$NPh\langle\begin{matrix}C_6H_4(Cl,HCl)\\ \text{———}\\ C_6H_4\end{matrix}\rangle CPh,$$

crystallises in golden needles; the *chloride*, $C_{25}H_{18}NCl$, prepared by the action of acetyl chloride on 5 : 10-diphenylacridol, crystallises with $1Me\cdot CO_2H$ and $2C_6H_6$ in yellow crystals, and with $2CHCl_3$ in yellow plates; it is also obtained by heating the hydrochlride in a vacuum at 150°, and does not melt at about 300°. W. H. G.

3 : 6-Dimethylfluoran. Enos Ferrario and M. Neumann (*Bull. Soc. chim.*, 1909, [iv], 5, 1098—1101. Compare Lambrecht, Abstr., 1909, i, 949).—3 : 6-Dimethylfluoran, m. p. 213·5° (corr.), has been obtained by the action of phthalyl chloride on *m*-cresol, and also in 80% yield by heating phthalic anhydride with *m*-cresol and zinc chloride. The compound is readily esterified by heating with alcoholic hydrogen chloride; on the addition of platinic chloride, the *platini-chloride*, $(C_{21}H_{16}OCl\cdot CO_2Et)_2PtCl_4$, separates. The *methyl* ester, $C_{21}H_{17}O\cdot CO_2Me$, has m. p. 115—116°.

The addition of bromine to a solution of dimethylfluoran in acetic acid results in the formation of an unstable, red oxonium *tribromide*. A *dibromo*-derivative, m. p. 249—250°, and a *tetrabromo*-derivative, m. p. 306°, have also been obtained. Dimethylfluoran forms a *tetranitro*-derivative, $C_{22}H_{12}O_{11}N_4$, and possibly a *dinitro*-derivative, m. p. 242°. The former decomposes at about 280°, and on reduction yields an amine, the *picrate* of which decomposes at 120—121°. W. O. W.

Preparation of 2 : 3-Diketodihydro-(1)-thionaphthen Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 213458. Compare Abstr., 1909, i, 950).—2 : 3-*Diketodihydro-1-thionaphthen-2-oxime* is prepared by adding sodium nitrite to a cooled solution of 3-oxy-1-thionaphthen in aqueous sodium hydroxide and subsequent acidification with dilute sulphuric acid. It forms yellow, silky prisms, m. p. 168°. The *acetyl* derivative, m. p. 168°, and the *phenylhydrazone*, m. p. 154°, are described.

On hydrolysing the preceding compound with 15% hydrochloric acid and reducing the colourless product with iron filings, it yields 2 : 3-diketodihydro-1-thionaphthen, the *phenylhydrazone* of which has m. p. 162°, and the *dianilino*-derivative, m. p. 80°.

The higher homologues of the foregoing compounds are similarly prepared, *3-oxy-5-methyl-(1)-thionaphthen* yielding 2 : 3-*diketo-5-methyl-*

dihydro-(1)-*thionaphthen*-2-*oxime*, m. p. 185°, and 5-*chloro*-3-*oxy*-(1)-*thionaphthen* gives 5-*chloro*-2 : 3-*diketodihydro*-1-*thionaphthen*-2-*oxime*, m. p. 188°. F. M. G. M.

Preparation of Derivatives of 2 : 3-Diketodihydro-(1)-thionaphthens. Badische Anilin- & Soda-Fabrik (D.R.-P. 214781).—Derivatives of 2 : 3-diketodihydro-(1)-thionaphthen have formerly been obtained by the action of aromatic amines on the dihalogenated derivatives of 3-ketodihydro-(1)-thionaphthen and hydrolysis of the product. It has now been found that nitroso-derivatives of aromatic amines will condense with 3-oxy-(1)-thionaphthen itself, giving rise to a condensation product which, on hydrolysis, furnishes the diketo-compound.

3-Oxy-(1)-thionaphthen in alcoholic or dilute alkali solution condenses at 40° with *p*-nitrosodimethylaniline, giving the *compound* (m. p. 176°), $C_6H_4\langle^{S-}_{CO}\rangle C{:}N{\cdot}C_6H_4{\cdot}NMe_2$. This product, when hydrolysed with 15% hydrochloric acid, gives 2 : 3-diketodihydro-(1)-thionaphthen.

p-Nitrosoethylaniline and *p*-nitrosodiphenylamine give similar products, melting at 158° and 193° respectively, which also undergo hydrolysis to furnish the diketone.

3-Oxy-5-methyl-(1)-thionaphthen, when submitted to this series of operations, yields 2 : 3-diketo-5-methyldihydro-1-thionaphthen, m. p. 143°. F. M. G. M.

Poly-membered Heterocyclic Systems containing Sulphur, and Ring Closure in the Para-Position. Wilhelm Autenrieth and Fritz Beuttel (*Ber.*, 1909, 42, 4346—4357).—It has been shown recently that dihydric mercaptans readily condense with aldehydes or ketones to form compounds containing six-, seven-, or sixteen-membered heterocyclic systems containing sulphur. The ease with which *o*-xylylene hydrosulphide reacts has suggested the use of the para-isomeride also.

p-Xylylene hydrosulphide, prepared by adding a boiling alcoholic solution of *p*-xylylene bromide to alcoholic potassium hydrosulphide saturated with hydrogen sulphide (compare Kötz, Abstr., 1900, i, 343), is separated by means of dilute aqueous sodium hydroxide from the simultaneously formed *monoethyl ether* of *p*-xylylene glycol,

$$C_{10}H_{14}O_2,$$

b. p. 250—252°. *p*-Xylylene hydrosulphide condenses, in the presence of hydrogen chloride, with aliphatic aldehydes or ketones to form only amorphous, rather indefinite products, but with aromatic aldehydes beautifully crystalline duplo-compounds are obtained, which are similar to those obtained from pentamethylene hydrosulphide (Autenrieth and Geyer, Abstr., 1909, i, 6). The duplo-compounds contain an eighteen-membered ring, and are very stable; nascent hydrogen does not cause the elimination of hydrogen sulphide or of the mercaptan; oxidising agents do not rupture the ring, and the compounds are stable to boiling alcoholic potassium hydroxide, but

undergo deep-seated changes by treatment with fuming hydrochloric acid at 180°.

Duplo-p-*xylylenebenzylidenemercaptal*,

$$C_6H_4<\begin{matrix}CH_2\cdot S\cdot CHPh\cdot S\cdot CH_2\\ CH_2\cdot S\cdot CHPh\cdot S\cdot CH_2\end{matrix}>C_6H_4,$$

m. p. 248—249°, is prepared by passing hydrogen chloride into an ice-cold mixture of equal molecular quantities of benzaldehyde and *p*-xylylene hydrosulphide. It crystallises in silvery leaflets, and has a molecular weight in naphthalene corresponding with its formula. In warm benzene it is oxidised by potassium permanganate and sulphuric acid to the *tetrasulphone*,

$$C_6H_4<\begin{matrix}CH_2\cdot SO_2\cdot CHPh\cdot SO_2\cdot CH_2\\ CH_2\cdot SO_2\cdot CHPh\cdot SO_2\cdot CH_2\end{matrix}>C_6H_4,$$

which melts above 300°.

Duplo-p-*xylylene*-p-*tolylidenemercaptal*, $C_{32}H_{32}S_4$, m. p. 266°, is prepared in a similar way, and yields a *tetrasulphone*, $C_{32}H_{32}O_8S_4$, m. p. 280—282° (decomp.). *Duplo*-p-*xylylene*-m-*tolylidenemercaptal*,

$$C_{32}H_{32}S_4,$$

m. p. 219—220°, is similarly obtained in almost theoretical yield. *Duplo*-p-*xylylene*-p-*hydroxybenzylidenemercaptal*, $C_{30}H_{28}O_2S_4$, m. p. 262—264° (decomp.), is prepared in ethereal solution, and yields a *dibenzoate*, m. p. 233°, by the Schotten-Baumann process.

Duplo-p-*xylylene*-m-*hydroxybenzylidenemercaptal*, $C_{30}H_{28}O_2S_4$, m. p. 251—252° (decomp.), is also prepared in ethereal solution, and forms a *dibenzoate*, m. p. 169°.

p-Xylylene hydrosulphide forms a *dibenzoate*, m. p. 135°, and a *dibenzyl thioether*, $C_6H_4(CH_2\cdot S\cdot C_7H_7)_2$, m. p. 65°. The latter in benzene solution is oxidised by potassium permanganate and sulphuric acid mainly to the corresponding *disulphone*, $C_{22}H_{22}O_4S_2$, m. p. 292—294° (decomp.); the accompanying *disulphoxide*,

$$C_6H_4(CH_2\cdot SO\cdot C_7H_7)_2,$$

m. p. 232—233°, is removed by acetone; it is more conveniently prepared by the addition of 30% hydrogen peroxide to a cold solution of the dibenzyl thioether in glacial acetic acid. C. S.

Poly-membered Heterocyclic Sytems containing Sulphur, and Ring Closure in the Meta-Position. Wilhelm Autenrieth and Fritz Beuttel (*Ber.*, 1909, 42, 4357—4361).—The following compounds are prepared by methods similar to those described in the preceding abstract.

m-Xylylene hydrosulphide forms a *dibenzoyl* derivative,

$$C_6H_4(CH_2\cdot SBz)_2,$$

m. p. 52·5°, and a *dibenzyl thioether*, m. p. 48°. m-*Xylylenedibenzyldisulphone*, $C_6H_4(CH_2\cdot SO_2\cdot C_7H_7)_2$, has m. p. 225°.

After many attempts with various aliphatic and aromatic aldehydes and ketones, the authors have succeeded in condensing *m*-xylylene hydrosulphide and acetone in the presence of hydrogen chloride, the crystalline product being the *duplo*-m-*xylenemercaptal* of *acetone*, $C_6H_4<\begin{matrix}CH_2\cdot S\cdot CMe_2\cdot S\cdot CH_2\\ CH_2\cdot S\cdot CMe_2\cdot S\cdot CH_2\end{matrix}>C_6H_4$, m. p. 254°, which is stable to alcoholic potassium hydroxide, nascent hydrogen, potassium perman-

ganate and sulphuric acid, and hydrogen peroxide; the corresponding *tetrasulphone*, $C_{22}H_{28}O_8S_4$, melts above 300°, and is insoluble in all known organic solvents. Its molecular weight is assumed, by analogy, to correspond with the preceding formula. C. S.

Crystalline Alkaloid of Calycanthus Glaucus. III. *iso*-Calycanthine, Isomeric with Calycanthine. Harry M. Gordin (*J. Amer. Chem. Soc.*, 1909, 31, 1305—1312).—In earlier papers (Abstr., 1905, i, 295; 1906, i, 35), calycanthine and its salts have been described.

On extracting the alkaloid from a new quantity of seed, a product was obtained which, although resembling calycanthine in composition and general appearance, differs from it in several important respects, and is therefore termed *iso*calycanthine. Whether the two samples of seed were derived from different species of *Calycanthus* or the difference between the alkaloids was due to a difference in the age of the plants is not at present known.

iso*Calycanthine*, $C_{11}H_{14}N_{2\cdot2}^{1}H_2O$, m. p. 212—214°, forms crystals of the bisphenoidal class of the orthorhombic system [$a : b : c = 1{\cdot}2557 : 1 : 1{\cdot}3226$], and has $[\alpha]_D$ 697·97°; the anhydrous alkaloid has m. p. 235—236°. The *hydrochloride*, *hydrobromide*, *hydriodide*, *platinichloride*, *aurichloride*, *nitrate*, *sulphate*, *hydrogen sulphate*, *picrate*, and *picrolonate* are described.

The *nitrosoamine*, $C_{11}H_{13}N_2{\cdot}NO$, darkens at 99° and melts at 106—107°. When the alkaloid is left with acetyl chloride for a few weeks, a steel-blue hydrochloride is produced, whilst if the mixture is heated for six hours in a sealed tube, a dark brown hydrochloride is formed. When treated with methyl iodide, the base is converted into its hydriodide, together with two other compounds which have not yet been investigated. If the alkaloid is digested with concentrated sulphuric acid, a product is obtained which is probably a sulphonic acid. E. G.

A New Highly Fluorescent Substance Derived from Physostigmine [Eserine]. Paul Gaubert (*Compt. rend.*, 1909, 149, 852—853).—When an aqueous solution of eserine is kept for several months, it acquires a deep blue tint, and on the addition of phthalic acid develops a red fluorescence which exceeds in intensity that of all known substances. The compound to which this is due has been isolated as dark blue crystals. W. O. W.

Constitution of Stachydrine. Ernst Schulze and G. Trier (*Ber.*, 1909, 42, 4654—4659. Compare Abstr., 1909, i, 323).—The constitution of stachydrine as the methylbetaine of hygric acid (dimethylbetaine of α-proline) is proved by its conversion into derivatives of hygric acid (Willstätter and Ettlinger, Abstr., 1903, i, 363) and its synthesis from this acid.

The *ethyl* ester of stachydrine hydrochloride forms a syrup, and yields a sparingly soluble *aurichloride*, $C_9H_{18}O_2NAuCl_4$, m. p. 59—60°. When distilled, the hydrochloride of the ester gives a 20% yield of ethyl hygrate, b. p. 77—79°/18 mm.

Stachydrine has been synthesised by converting ethyl hygrate

(ethyl 1-methylpyrrolidine-2-carboxylate) into its methiodide (Willstätter and Ettlinger, *loc. cit.*, 364), and then treating this with silver oxide.

Stachydrine platinichloride, $2C_7H_{13}O_2N,H_2PtCl_6$, crystallises in long, yellow needles. J. J. S.

Synthesis of Indolenine Ketones. Giuseppe Plancher and D. Giumelli (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 393—397).—3 : 3-Dimethylindolenine-2-carboxylonitrile, $C_6H_4<^{\text{---N}}_{CMe_2}>C\cdot CN$, previously described as a liquid (Abstr., 1899, i, 543), has been obtained in the solid state, m. p. about 38°.

3 : 3-*Dimethylindolenyl* 2-*methyl ketone*, $C_6H_4<^{\text{---N}}_{CMe_2}>C\cdot COMe$, prepared by the action of magnesium methyl iodide on the preceding compound, forms volatile needles, m. p. 130°, is readily resinified by acids, and gives the iodoform reaction with iodine and alkali. With hydroxylamine it gives the oxime, m. p. 175—176°, formed by the action of nitrous acid on 3 : 3-dimethyl-2-ethylindolenine (compare Abstr., 1903, i, 433). The corresponding *semicarbazone*, $C_{13}H_{16}ON_4$, forms scales, m. p. 242°.

The action of magnesium phenyl bromide on 3 : 3-dimethylindolenine-2-carboxylonitrile yields, not a ketone, but the *imino*-compound, $C_6H_4<^{\text{---N}}_{CMe_2}>C\cdot CPh{:}NH$, m. p. 103·5°. This imino-derivative is the first intermediate compound formed in Blaise's reaction (Abstr., 1901, i, 133), which proceeds according to the equations: (1) $R\cdot CN + MgR_1Br = CRR_1{:}NMgBr$; (2) $CRR_1{:}NMgBr + H_2O = CRR_1{:}NH + MgBr\cdot OH$, and (3) $CRR_1{:}NH + H_2O = R\cdot CO\cdot R_1 + NH_3$. The above imino-compound does not readily give phase (3) of the reaction, but the imino-group present reacts easily with ketone reagents; thus, the compound gives an *oxime*, $C_{17}H_{16}ON_2$, which forms prisms, m. p. 205°, and a *p-nitrophenylhydrazone*, m. p. 209°.

T. H. P.

Catalytic Hydrogenation of Aromatic and Quinoline Bases. Georges Darzens (*Compt. rend.*, 1909, **149**, 1001—1004. Compare Padoa, Abstr., 1906, i, 765; Ipatieff, Abstr., 1908, i, 332).—1 : 2 : 3 : 4-Tetrahydroquinoline is formed when quinoline is hydrogenated at 160—180° in presence of nickel which has been obtained by reduction of its hydroxide at 250—255°. The product is free from indolé and from more highly hydrogenated quinolines. 6-Methyltetrahydroquinoline has been obtained in the same way.

The reduction products of dimethyl- and diethyl-aniline have been investigated by Senderens (Abstr., 1904, i, 660), but have been obtained by the present author in a state of greater purity. *cyclo*-Hexyldimethylamine has b. p. 159°, and forms a *picrate*, m. p. 176—177°; the corresponding diethyl derivative has b. p. 191°, and forms a *picrate*, m. p. 91—92°.

Attention is drawn to the influence of the temperature at which the nickel is prepared on its behaviour as a catalyst. W. O. W.

Bz-Sulphoquinolinecarboxylic Acids. Albert Edinger and L. Bühler (*Ber.*, 1909, 42, 4313—4320).—In connexion with their work on *Bz*-quinoline mercaptans (Abstr., 1908, *i*, 363) the authors have prepared the following substances.

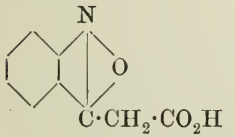
5-*Sulphoquinoline*-8-*carboxylic acid*, $CO_2H \cdot C_9NH_5 \cdot SO_3H$, is obtained by oxidising 8-methylquinoline-5-sulphonic acid (Herzfeld, Abstr., 1884, 1198) by chromic and sulphuric acids, and is separated from the unchanged material by crystallisation from dilute sulphuric acid, D 1·16, at 75°; the *copper* and the *barium* salts are mentioned.

6-Methylquinoline-7-sulphonic acid has been prepared by the Skraup reaction, but is obtained in good yield by working under the author's conditions. When heated at 260—270° with a mixture of equal parts of potassium and sodium hydroxides and a little water, it yields 7-*hydroxy*-6-*methylquinoline*, m. p. 244°, b. p. 240°/22 mm., whilst by distilling its sodium salt with potassium cyanide, 7-*cyano*-6-*methylquinoline*, m. p. 133°, is obtained. 7-*Sulphoquinoline*-6-*carboxylic acid* is obtained from 6-methylquinoline-7-sulphonic acid by oxidation with chromic and sulphuric acids; it crystallises in white octahedra, and the *strontium* and *barium* salts are mentioned. By fusion with equal parts of potassium and sodium hydroxides at 275°, a *dihydroxyquinoline*, darkening at 280° and m. p. 321°, is obtained, which crystallises in large, yellow needles, and contains its hydroxyl groups in positions 6 and 7, assuming that intramolecular change has not occurred during the fusion with the alkalis.

8-*Sulphoquinoline*-6-*carboxylic acid* and 6-*sulphoquinoline*-8-*carboxylic acid* are obtained from the corresponding toluquinolinesulphonic acids by processes of oxidation similar to the preceding.

The reaction between sodium 6-sulphoquinoline-8-carboxylate and phosphorus pentachloride at 125—135° yields the sulphonyl chloride, which is reduced by stannous chloride and hydrochloric acid; the resulting tin double salt is decomposed by sodium hydroxide, yielding the corresponding mercaptide, which is converted by the Schotten-Baumann process into the *benzoyl* derivative, m. p. 213°, of quinoline-6-mercaptan-8-carboxylic acid. C. S.

Reduction of *o*-Nitrophenylpropiolic Acid. Gustav Heller and Walter Tischner (*Ber.*, 1909, 43, 4555—4566).—On reduction of *o*-nitrophenylpropiolic acid, indigotin and *o*-aminophenylpropiolic acid have been obtained. When reduction is carried out with zinc dust in ammoniacal solution, a ring compound, *homoanthroxanic acid* (annexed formula), is formed. This crystallises in lustrous, flat needles with a faint yellow shimmer; m. p. 108°. It is a strong carboxylic acid; the alcoholic-aqueous solution reddens litmus; it dissolves in presence of sodium and barium carbonates and sodium acetate. The *silver* salt contains one atom of metal. It is not easily esterified or acetylated, reduces ammoniacal silver and Fehling's solutions on boiling, and gives no coloration with ferric chloride.



When heated at 110—120° it is converted into methylanthroxane, $C_6H_4<\begin{matrix}N\text{—}\\ |\\ CMe\end{matrix}>O$. Sodium nitrite converts it into the *oxime* of anthroxanaldehyde, $\begin{matrix}N\text{—}O\\ |\ \diagdown\ |\\ C_6H_4\cdot C\cdot CH{:}N\cdot OH\end{matrix}$, crystallising in colourless needles, m. p. 172—173°, which can also be prepared from anthroxanaldehyde and hydroxylamine.

On reduction, homoanthroxanic acid at first forms *o*-aminobenzoylacetic acid, which immediately condenses to the anhydride, 4-ketohydrocarbostyril, $C_6H_4<\begin{matrix}N{=}C\cdot OH\\ |\\ CO\cdot CH_2\end{matrix}$, which crystallises in bunches of colourless, hexagonal plates, and is identical with the 4-hydroxycarbostyril described by Baeyer and Bloem (Abstr., 1883, 196); the benzoyl derivative forms radially-grouped, colourless needles, m. p. 220°.

Homoanthroxanic acid, when warmed with hydrochloric acid, is converted into 2 : 3-*dihydroxy*-4-*quinolone*, $C_6H_4<\begin{matrix}NH\cdot C\cdot OH\\ ||\\ CO\text{—}C\cdot OH\end{matrix}$ or $C_6H_4<\begin{matrix}N{=}C\cdot OH\\ |\\ CO\cdot CH\cdot OH\end{matrix}$, which forms long, colourless needles, m. p. 276° (decomp.), and gives a characteristic, stable, violet coloration with ferric chloride. The *benzoyl* derivative crystallises in colourless, matted needles, m. p. 216—217° (decomp.). On treatment with phosphorus pentachloride, two crystalline products are obtained: needles, m. p. 85°, volatile in steam, and non-volatile needles, m. p. 205—220°. It is converted into 4-ketohydrocarbostyril on reduction.

E. F. A.

Condensation of α-Diketones with Aldehydes and Primary Arylamines. Walther Borsche and J. Camper Titsingh (*Ber.*, 1909, **42**, 4283—4287. Compare Abstr., 1909, i, 955).—When α-diketones are allowed to react with aldehydes and arylamines under conditions similar to those used in the preparation of cinchonic acids from pyruvic acid, aldol condensation occurs (in one case 2 molecules of the aldehyde reacting with one of the ketone), and the resulting product forms an anil with the arylamine. Thus aniline, benzaldehyde, and acetylbenzoyl (Abstr., 1907, i, 326) react in hot alcoholic solution, yielding *αγ-dihydroxy-αγ-diphenyl-β-phenylglyoxylpropane-dianil*, $NPh{:}CPh\cdot C(:NPh)\cdot CH(CHPh\cdot OH)_2$, which crystallises from glacial acetic acid in yellow needles, m. p. 176° (decomp.). When heated with acetic anhydride and anhydrous sodium acetate, the anil yields an *acetyl* derivative, $C_{37}H_{30}O_2N_2$, probably

$$NPh{:}CPh\cdot C(:NPh)\cdot C(:CHPh)\cdot CHPh\cdot OAc,$$

which crystallises in colourless needles, m. p. 273°.

When salicylaldehyde is substituted for benzaldehyde in the above condensation, a resin is formed, but with anisaldehyde, *δ-phenyl-α-anisyl-Δ$^{\alpha}$-butene-γδ-dianil*, $NPh{:}CPh\cdot C(:NPh)\cdot CH{:}CH\cdot C_6H_4\cdot OCH_3$, is formed, crystallising in needles, m. p. 153°.

m-Nitrobenzaldehyde yields a similar *anil*,

$$NPh{:}CPh{\cdot}C(:NPh){\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2,$$

in the form of yellow needles, m. p. 181°.

α-Phenyl-δ-anisyl-Δ$^{\alpha}$-butene-γδ-dianil,

$$OMe{\cdot}C_6H_4{\cdot}C(:NPh){\cdot}C(:NPh){\cdot}CH{:}CHPh,$$

obtained from aniline, benzaldehyde, and acetyl-*p*-anisoyl, forms colourless needles, m. p. 203°. When *p*-anisidine is substituted for aniline, the p-*anisil*,

$$OMe{\cdot}C_6H_4{\cdot}C(:N{\cdot}C_6H_4{\cdot}OMe){\cdot}C(:N{\cdot}C_6H_4{\cdot}OMe){\cdot}CH{:}CHPh,$$

is obtained as yellow needles, m. p. 158°.

Dicinnamoyldianil, $CHPh{:}CH{\cdot}C(:NPh){\cdot}C(:NPh){\cdot}CH{:}CHPh$, obtained from diacetyl, benzaldehyde, and aniline in glacial acetic acid solution, forms a yellow, crystalline powder, m. p. 270°.

Acetylbenzoyl, benzaldehyde, and *m*-nitroaniline do not condense.

J. J. S.

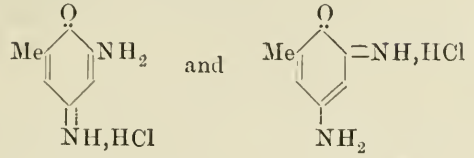
Auxochromic Action of Amino- and Aminophenyl Groups. Jean Piccard (*Ber.*, 1909, 42, 4332—4341).—The intense colour of Wurster's salts and of many dyes, particularly of the triphenylmethane series, is attributed by Willstätter and Piccard (Abstr., 1908, i, 475) to the *meri*-quinonoid constitution of such substances. This view is contraverted by Kehrmann (Abstr., 1908, i, 699), who maintains, in consequence of the behaviour of the aminobenzoquinoneimines (Abstr., 1906, i, 967), that the intense colour is due to the influence of a quinonoid benzene nucleus increased by an auxochromic amino-group. The author shows that by oxidising 3 : 5-diamino-*o*-cresol dihydrochloride in a freezing mixture by an excess of ferric chloride, and adding a saturated solution of potassium nitrate, a light red *holo*-quinonoid *amino-o-toluquinoneimine nitrate*, $C_7H_9O_4N_3$, is obtained, which does not show any resemblance to true red dyes in its behaviour in light. When the oxidation is performed with a deficiency of ferric chloride, a dark red *meri*-quinonoid compound is obtained. Also, in solution, Kehrmann's red compounds (*loc. cit.*) differ essentially from red dyes; the latter exhibit pronounced selective absorption, whilst the former show no trace of a band.

Coloured quinonoid substances are classified in two groups: (1) Colour is due to a quinonoid nucleus and an auxochromic amino-group; (2) colour is due to the junction of quinonoid and hydroquinonoid nuclei (*meri*-quinonoid compounds). The preceding light red nitrate is typical of group (1), Wurster's red salt of group (2).

The difference in the colour of triphenylmethaneimine bases and their salts is attributed by Kehrmann to a change in the constitution of the chromophore. From the spectroscopic examination of magenta, the author considers that the triphenylmethane dyes are *meri*-quinonoid compounds belonging to group (2). Substances which contain only an auxochromic amino-group in addition to the quinonoid nucleus are not dyes.

When an aqueous solution of diaminocresol dihydrochloride is oxidised by an excess of ferric chloride in the presence of saturated sodium chloride, a light red aminotoluquinoneimine hydrochloride crystallises at −15°, and a dark red isomeride at the ordinary

temperature. The former is regarded as the *p*-quinonoid and the latter as the *o*-quinonoid form respectively :



C. S

A Reaction of Polybasic Acids and a New Reaction for Titanium. Jean Piccard (*Ber.*, 1909, 42, 4341—4345).—It is well known that the reduction of organic substances by titanous chloride is accelerated by the addition of potassium sodium tartrate. The author finds that indigotin, Wurster's red, and, in particular, aminotoluquinoneimine hydrochloride (preceding abstract) are very slowly affected by titanous chloride in aqueous or dilute hydrochloric acid solution, but the addition of certain acids, such as tartaric acid, increases the rate of reduction enormously. An examination of about fifty inorganic and organic acids reveals the fact that, in general, polybasic acids exert an accelerative influence, but not so monobasic acids. The most marked effect is produced by hydrofluoric acid (an argument in favour of the polymerised state, H_2F_2), oxalic, glycollic, lactic, pyruvic, tartaric, malic, and citric acids, catechol, and pyrogallol. The remaining halogen acids, and formic, acetic, propionic, butyric, benzoic, β-naphthoic, and monochloroacetic acids have no influence.

Catechol produces with a solution of titanous chloride a yellowish-orange coloration, which is much more intense than that produced by oxalic acid. The test, which is fifteen times more sensitive than the hydrogen peroxide test, should be performed with an excess of catechol and in the absence of mineral acids, and preferably also of alkali hydroxides and carbonates and ammonium hydroxide.

The author suggests that Fenton's brown substance, obtained from dihydroxymaleic acid and compounds of quadrivalent titanium (Trans., 1908, **93**, 1064), may contain tervalent titanium. C. S.

Diketodialkylpiperazines. Karl W. Rosenmund (*Ber.*, 1909, 42, 4470—4481).—The author has prepared a number of diketodialkylpiperazines in order to investigate the hypnotic action of the alkyl groups, more especially of the ethyl group, in them. 2 : 5-Diketo-6 : 6-diethylpiperazine exhibits no such action, although, like veronal, it contains two ethyl groups combined with a quaternary carbon atom occurring in a physiologically indifferent ring-system.

α-Bromo-α-ethylbutyric acid (compare Kalle & Co., Abstr., 1907, i, 276) forms white scales, m. p. 20°, b. p. 130—133°/18 mm., and may be prepared in almost theoretical yield by the action of bromine on α-ethylbutyric acid in a sealed tube at 136—140°. Its *ethyl* ester is a colourless liquid, b. p. 87—88°/18 mm. (impure), with an intense camphor-like odour.

α-Amino-α-ethylbutyric acid (compare Gulewitsch and Wasmus, Abstr., 1906, i, 409) is best prepared by the action of methyl-alcoholic

ammonia on α-bromo-α-ethylbutyric acid, its preparation from diethyl ketone by Zelinsky and Stadnikoff's method (Abstr., 1906, i, 425) being difficult and infertile. Its *ethyl* ester, $NH_2 \cdot CEt_2 \cdot CO_2Et$, is a colourless oil, b. p. 76—77°/15 mm.

α-Chloroacetylamino-α-methylbutyric acid,

$$CH_2Cl \cdot CO \cdot NH \cdot CMeEt \cdot CO_2H,$$

prepared by the action of chloroacetyl chloride and sodium hydroxide on α-amino-α-methylbutyric acid, forms colourless needles, m. p. 162°.

α-Glycylamino-α-methylbutyric acid, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CMeEt \cdot CO_2H$, prepared by the action of aqueous ammonia on α-chloroacetylamino-α-methylbutyric acid, forms white needles, m. p. 245° (decomp.).

3 : 6-*Diketo*-2-*methyl*-2-*ethylpiperazine*, $CMeEt\langle^{CO \cdot NH}_{NH \cdot CO}\rangle CH_2$, prepared by the action of ammonia either on a methyl-alcoholic solution of ethyl α-glycylamino-α-methylbutyrate at 0°, or on ethyl α-chloroacetylamino-α-methylbutyrate at 100°, forms slender, white needles, m. p. 250°.

3 : 6-*Diketo*-2 : 5-*dimethyl*-2 : 5-*diethylpiperazine*,

$$CMeEt\langle^{CO \cdot NH}_{NH \cdot CO}\rangle CMeEt,$$

prepared by heating ethyl α-amino-α-methylbutyrate in a sealed ube at 240—250°, forms slender needles, subliming on heating, and having m. p. 336° in a closed capillary tube.

α-Chloroacetylamino-α-ethylbutyric acid, $CH_2Cl \cdot CO \cdot NH \cdot CEt_2 \cdot CO_2H$, forms small needles or prisms, m. p. 190°.

α-Glycylamino-α-ethylbutyric acid, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CEt_2 \cdot CO_2H$, forms white crystals, m. p. 269° (decomp.).

3 : 6-*Diketo*-2 : 2-*diethylpiperazine*, $CEt_2\langle^{CO \cdot NH}_{NH \cdot CO}\rangle CH_2$, prepared by the action of methyl-alcoholic ammonia at 105° on ethyl α-chloroacetylamino-α-ethylbutyrate, forms long, shining needles, m. p. 272°, having an extremely bitter taste.

Ethyl α-glycylamino-α-ethylbutyrate, m. p. 202—210°, when heated with alcoholic ammonia at 100°, yields only the corresponding free acid, m. p. 269°. This result is not in accord with Fischer's views on the mechanism of the formation of the anhydrides of amino-acids from the esters of halogen-acylamino-acids by the action of ammonia, since, according to these views, the dipeptide esters are formed as intermediate products and give the anhydrides by loss of alcohol. It seems, on the contrary, that the alkoxy-group is first replaced by an amino-group, the amide thus formed losing hydrogen chloride and giving the anhydride:

$$CH_2Cl \cdot CO \cdot NH \cdot CEt_2 \cdot CO_2R \longrightarrow CH_2Cl \cdot CO \cdot NH \cdot CEt_2 \cdot CO \cdot NH_2 \longrightarrow CEt_2\langle^{CO \cdot NH}_{NH \cdot CO}\rangle CH_2.$$

That such an intermediate amide can be formed is shown by the action of ammonia on the ethyl ester of bromodiethylacetylglycine (*vide infra*).

Ethyl bromoethylbutyrylaminoacetate, $CEt_2Br \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, prepared by the action of bromoethylbutyryl chloride on ethylaminoacetate, has m. p. 35—36°

Bromoethylbutyrylglycinamide, $CEt_2Br\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, obtained by the action of methyl-alcoholic ammonia on the preceding ester, has m. p. 109—110°. This compound exhibits little inclination to ring-closure, and on heating for several hours with methyl-alcoholic ammonia at 100—105°, it yields (1) two isomeric compounds, m. p. 122° and 87—88°, which are apparently the two stereoisomeric *α*-ethylcrotonylglycinamides, $CHMe{:}CEt\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$ (compare Mannich and Zernik, Abstr., 1908, i, 399), and (2) small quantities of two compounds, m. p. 99—100° and 110° respectively. With pyridine in place of ammonia, a similar reaction occurs.

T. H. P.

Pyrimidines. XLVIII. Synthesis of 5-Cyanouracil. Treat B. Johnson (*Amer. Chem. J.*, 1909, 42, 505—515).—The work described in this paper was undertaken for the purpose of preparing certain pyrimidines to be used for the synthesis of new thymine derivatives. It has been shown by Wheeler, Johnson, and Johns (Abstr., 1907, i, 559) that ethyl ethoxymethylenemalonate condenses with *ψ*-thiocarbamides with formation of esters of 2-alkylthiol-6-pyrimidone-5-carboxylic acids, which are readily hydrolysed by hydrochloric acid with production of uracil-5-carboxylic acid. It therefore seemed probable that 5-cyanouracil could be obtained in an analogous manner from ethyl cyanoethoxymethyleneacetate. Experiments have been carried out which show that ethyl-*ψ*-thiocarbamide condenses with this ester in presence of alkali hydroxide with formation of 5-cyano-2-ethylthiol-6-pyrimidone, together with smaller quantities of ethyl 6-amino-2-ethylthiolpyrimidine-5-carboxylate (Wheeler and Johns, Abstr., 1907, i, 1083). On hydrolysing the former product with sulphuric acid, a quantitative yield of 5-cyanouracil is obtained.

On adding ethyl cyanoethoxymethyleneacetate (1 mol.) to an alcoholic solution of ethyl-*ψ*-thiocarbamide (1 mol.), *ethyl α-cyano-β-ethyl-ψ-thiocarbamidoacrylate*, $NH_2\cdot C(SEt){:}N\cdot CH{:}C(CN)\cdot CO_2Et$, m. p. 130° (decomp.), separates in yellow crystals, and, when warmed with alkali hydroxide, is converted into *5-cyano-2-ethylthiol-6-pyrimidone*, $NH\langle\begin{matrix}C(SEt)=N\\CO\cdot C(CN)\end{matrix}\rangle CH$, m. p. 222°, which crystallises in prisms. If ethyl cyanoethoxymethyleneacetate (1 mol.) is added to an alcoholic solution of ethyl-*ψ*-thiocarbamide (1·7 mols.), *α-cyano-β-ethyl-ψ-carbamidoacrylethyl-ψ-thiocarbamide*,

$$NH_2\cdot C(SEt){:}N\cdot CH{:}C(CN)\cdot CO\cdot N{:}C(SEt)\cdot NH_2,$$

m. p. 164—165° (decomp.), is produced, which crystallises in prisms; this compound is converted by warm sodium hydroxide into 5-cyano-2-ethylthiol-6-pyrimidone and by concentrated hydrochloric acid into 5-cyanouracil.

5-Cyanouracil (2 : 6-*diketo-5-cyanopyrimidine*),

$$NH\langle\begin{matrix}CO---NH\\CO\cdot C(CN)\end{matrix}\rangle CH,$$

m. p. 295° (decomp.), crystallises in prisms, and by the action of concentrated hydrochloric acid is converted quantitatively into uracil.

When 5-cyano-2-ethylthiol-6-pyrimidone is dissolved in concentrated

hydrochloric acid and the solution evaporated to dryness at 100°, 5-cyanouracil is produced, together with *uracil-5-carboxylamide*,

$$NH<^{CO\text{---------}NH}_{CO\cdot C(CO\cdot NH_2)}>CH,$$

which forms small prisms, does not melt below 300°, and is converted quantitatively into uracil by concentrated hydrochloric acid. E. G.

Influence of Constitution on the Conversion of Phenylhydrazones of Unsaturated Compounds into Pyrazolines. Karl Auwers and H. Voss (*Ber.*, 1909, **42**, 4411—4427).—The method recently described for converting into pyrazolines the phenylhydrazones of unsaturated aldehydes and ketones of the type

$$R\cdot CH{:}CH\cdot CO\cdot R'$$

(Abstr., 1909, i, 59) is now employed to determine how far the readiness to undergo this change is affected by the constitution of the groups R and R'. This paper deals with the aromatic unsaturated aldehydes and ketones. The phenylhydrazone of phenyl styryl ketone changes into 1 : 3 : 5-triphenylpyrazoline even at low temperatures, and cannot be isolated; the phenylhydrazones of cinnamaldehyde and styryl methyl ketone, however, only form pyrazolines at a high temperature. The phenylhydrazones of the following ketones are stable: styryl ethyl ketone, styryl *n*-propyl ketone, styryl *n*-butyl ketone, styryl *n*-nonyl ketone; those of styryl *iso*propyl ketone and styryl *tert.*-butyl ketone are unstable, especially the latter. Hence the structure of the group R', rather than its weight, seems of importance.

The introduction of an hydroxyl or methoxy-group into the ortho-position in one of the benzene nuclei favours the formation of pyrazolines. From *o*-hydroxystyryl ethyl and propyl ketones only the pyrazolines can be obtained. *o*-Methoxystyryl ethyl ketone and phenylhydrazine also yield a pyrazoline directly. The introduction of a nitro-group has the opposite effect: phenyl *m*- and *p*-nitrostyryl ketones yield phenylhydrazones which are converted into pyrazolines only on boiling with glacial acetic acid. The *p*-nitrophenylhydrazone of cinnamaldehyde cannot be converted into a pyrazoline even by means of this reagent. Furfurylideneacetone behaves like styryl methyl ketone. Cinnamylideneacetophenone yields a stable phenylhydrazone.

For distinguishing between phenylhydrazones and pyrazolines, Knorr's reaction is not to be depended on in every case; reduction with sodium amalgam is a safer criterion; under this treatment all phenylhydrazones yield aniline. *Cinnamaldehyde-p-bromophenylhydrazone* forms yellow needles, m. p. 139—140°; when boiled with glacial acetic acid it yields *5-phenyl-1-p-bromophenylpyrazoline*, which crystallises in yellow needles, m. p. 140°. 1 : 5-Diphenyl-3-methylpyrazoline (from styryl methyl ketone) has m. p. 115—116° (Knorr gave 109°: Abstr., 1885, 555). Styryl ethyl ketone-phenylhydrazone has m. p. 104—105° (Harries and Müller gave 101°: Abstr., 1902, i, 295).

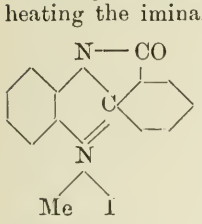
1 : 5-*Diphenyl-3* : 4 *dimethylpyrazoline*, prepared from α methyl styryl

ethyl ketone-phenylhydrazone, has m. p. 82—83°. *Styryl* iso*propyl ketone* has b. p. 147°/11 mm.; the 1 : 5-*diphenyl*-3-iso*propylpyrazoline* obtained from it forms white needles, m. p. 88·5°. *Styryl* n-*butyl ketone* has b. p. 159—167°/11 mm., and m. p. 38—39°; the *phenylhydrazone* has m. p. 97·5—98·5°. 1 : 5-*Diphenyl*-3-tert.-*butyl pyrazoline* (from styryl *tert.*-butyl ketone) has m. p. 108—108·5°. *Styryl* n-*nonyl ketone-phenylhydrazone* crystallises in silky, felted needles, m. p. 76—77°; when heated with glacial acetic acid it gives a *pyrazoline* in brown crystals, m. p. 60°. *o*-Hydroxystyryl ethyl ketone has m. p. 118—119° (Decker and von Fellenberg, Abstr., 1909, i, 116, give 101°); with phenylhydrazine, it yields directly 1-*phenyl*-5-o*hydroxyphenyl*-3-*ethylpyrazoline*, which crystallises in small needles, m. p. 134°. The substance of m. p. 119°, which Harries and Busse (Abstr., 1896, i, 301) obtained from *o*-hydroxystyryl *n*-propyl ketone, is not, as they assumed, the phenylhydrazone, but 1-*phenyl*-5-o-*hydroxyphenyl*-3-*propylpyrazoline*. When heated with glacial acetic acid it yields a *compound*, m. p. 98—99°, which does not give the pyrazoline reaction. The supposed phenylhydrazone, obtained by the same authors (*loc. cit.*) from phenyl-*o*-hydroxystyryl ketone, is 1 : 3-*diphenyl*-5-o-*hydroxyphenylpyrazoline*; it yields a *mono-benzoyl* derivative, m. p. 172°. o-*Methoxystyryl ethyl ketone*, a yellow oil, gives 1-*phenyl*-5-o-*methoxyphenyl*-3-*methylpyrazoline*, which forms yellow needles, m. p. 87—88°. p-*Nitrostyryl methyl ketone-phenylhydrazone* forms red crystals, m. p. 195—196°; when heated with glacial acetic acid, it yields 1-*phenyl*-5-p-*nitrophenyl*-3-*methylpyrazoline*, which crystallises in small, golden-yellow needles, m. p. 112—113°. *Phenyl*-m-*nitrostyryl ketone-phenylhydrazone* has m. p. 101—103°; boiling glacial acetic acid converts it into 1 : 3-*diphenyl*-5-m-*nitrophenylpyrazoline*, which forms brownish-yellow needles, m. p. 122—123°. *Phenyl* p-*nitrostyryl ketone-phenylhydrazone* crystallises in felted, red needles, m. p. 138—139°; it yields 1 : 3-*diphenyl*-5-p-*nitrophenylpyrazoline*, which forms brownish-yellow needles, m. p. 113—114°. Furfurylideneacetone has b. p. 112—115°/10 mm.; its *phenylhydrazone* forms yellow needles, m. p. 131—132°; 1-*phenyl*-5-*furyl*-3-*methylpyrazoline* crystallises in large, white needles, which are volatile in steam, and have m. p. 102—103°. Cinnamylideneacetophenonephenylhydrazone has m. p. 156—158° (Sorge, Abstr., 1902, i, 379, gave 125—126°). R. V. S.

Benzoylenebenziminazole. Hans Rupe and K. G. Thiess [and, in part, with Alex. Wetter] (*Ber.*, 1909, **42**, 4287—4304).—*o*-Benzoylenebenziminazole (Thiele and Falk, Abstr., 1906, i, 751) can be prepared by reducing *o*-nitrophthalanil with stannous chloride and hydrochloric acid, or, better (75% of theory), with iron and acetic acid. It crystallises in long, yellow needles with a silky lustre, m. p. 212—213°, and is readily hydrolysed by acids or alkalis to phenylbenziminazole-*o*-carboxylic [benziminazole-2-benzoic] acid, m. p. 266° (Thiele and Falk, 273°). The *hydrochloride* of the acid forms long, lustrous needles. The *methyl* ester, $C_{15}H_{12}O_2N_2$, crystallises in glistening, colourless needles, m. p. 188°. The *aurichloride* of the ethyl ester, $C_{16}H_{15}O_2N_2,AuCl_4$, forms slender, orange-yellow needles, m. p. 120°. When the ethyl ester is

heated, it yields alcohol and the iminazole. The *phenylhydrazide* of the acid, $C_6H_4<^{NH}_{N}>C\cdot C_6H_4\cdot CO\cdot NH\cdot NHPh$, crystallises in colourless needles, m. p. 244°.

Benzoylenebenziminazole methiodide (annexed formula), obtained by heating the iminazole with excess of methyl iodide in sealed tubes at 90—100°, crystallises in slender, bright red needles, m. p. about 200°. When carefully heated above its m. p., it yields methyl iodide and the benziminazole, and when boiled with water yields *benziminazole-2-benzoic acid methiodide*, $C_6H_4<^{NH}_{N(MeI)}>C\cdot C_6H_4\cdot CO_2H$, which crystallises in glistening, yellow cubes, m. p. 200—210°.



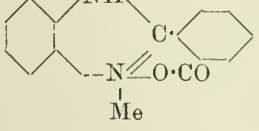
The *methiodide* of the methyl ester, $C_{16}H_{15}O_2N_2I$, is obtained by the action of methyl alcohol on the red methiodide at 90—100°. The *methiodide* of *methyl* 1-*methylbenziminazole*-2-*benzoate*,

$$C_6H_4<^{NMe}_{N(MeI)}>C\cdot C_6H_4\cdot CO_2Me,$$

obtained (*a*) by heating benzoylenebenziminazole with excess of methyl iodide and a little methyl alcohol at 120°, (*b*) by heating the methyl ester of the acid with methyl iodide (2 mols.) and a little methyl alcohol at 100°, or (*c*) by heating the methiodide of the methyl ester with methyl iodide at 100°, crystallises in large, compact prisms, m. p. 230°.

The *methiodide* of the ethyl ester, $C_{17}H_{17}O_2N_2I$, forms compact prisms, m. p. 191°. The *methiodide* of *ethyl* 1-*methylbenziminazole*-2-*benzoate*, $C_{18}H_{19}O_2N_2I$, crystallises in colourless needles or long prisms, m. p. 175°.

When heated with ammonium hydroxide solution or with sodium acetate solution at the ordinary temperature, the methiodide of the 2-benzoic acid yields the *betaine* (annexed formula), which crystallises in minute needles, m. p. 280—281°. Its constitution as a betaine is based on the following properties: it dissolves readily in alkali carbonate solutions, and the addition of hydrochloric acid precipitates the methochloride of benziminazole-2-benzoic acid. When heated with acetic anhydride and hydriodic acid, it yields the red methiodide of benzoylenebenziminazole. When heated for some time at 280—290°, it yields benzoylenebenziminazole, methyl alcohol, and unaltered substance.



The *methochloride* of benziminazole-2-benzoic acid, $C_{15}H_{13}O_2N_2Cl$, crystallises in colourless needles, m. p. 272—274°, and with acetic anhydride yields *benzoylenebenziminazole methochloride*, $C_{15}H_{11}ON_2Cl$, greenish-yellow needles, m. p. 200°. The *methobromide* of the acid, $C_{15}H_{13}O_2N_2Br$, has m. p. about 270°, and the *methobromide* of the benzoylenebenziminazole forms yellow needles, m. p. about 230°. When the methiodide of methyl 1-methylbenziminazole-2-benzoate is shaken with moist silver oxide, the corresponding *ammonium* base, $C_{17}H_{18}O_3N_2$, is obtained as a white solid, m. p. 252°.

When benzoylenebenziminazole is covered with nitric acid (D 1·52) and acetic anhydride is added, drop by drop, at 0°, a *nitro*-derivative, I, $C_{14}H_7O_3N_3$, which crystallises in pale yellowish-green needles, m. p. 239°, is formed, together with *nitrobenziminazole-2-benzoic acid*, $C_{14}H_9O_4N_3$, colourless needles, m. p. 280—300° (decomp.).

An isomeride, *nitrobenzoylenebenziminazole*, II, is formed when nitric acid (D 1·25) is added to a solution of the iminazole in acetic anhydride; it crystallises in small, brown needles, m. p. 280° (decomp.), and is accompanied by a nitrobenziminazole-2-benzoic acid, which crystallises in orange-coloured needles, m. p. 280—300° (decomp.). This second nitro-acid is a powerful dye.

Aminobenzoylenebenziminazole, I, $C_{14}H_9ON_3$, obtained by reducing the nitro-compound, I, with sodium hyposulphite, crystallises in brilliant red, flat needles, m. p. 298—305°. Its *acetyl* derivative, $C_{16}H_{11}O_2N_3$, forms yellow needles, decomposing at 253°. The base is a dye, and when diazotised and coupled with phenols yields valuable azo-dyes.

o-Nitrophthalanil, $NO_2{\cdot}C_6H_4{\cdot}N{:}C_2O_2{:}C_6H_4$, obtained by condensing *o*-nitroaniline and phthalic anhydride with sodium acetate, crystallises in pale yellow needles, m. p. 203°. It is stable towards acids, but is readily decomposed by alkalis, and when reduced with a concentrated sodium hyposulphite solution yields *o-aminophthalanil*, $NH_2{\cdot}C_6H_4{\cdot}N{:}C_2O_2{:}C_6H_4$, which crystallises in brilliant yellow needles, m. p. 188—189°. The *acetyl* derivative, $C_{16}H_{12}O_3N_2$, forms colourless needles, m. p. 202°; the *hydrochloride*, glistening, colourless needles. When diazotised and coupled with resorcinol, the base yields an *azo-dye*, $C_{20}H_{13}O_4N_3$, as golden-brown plates, m. p. 190°. J. J. S.

Indigotin. II. Indigotin Diarylimides. Eugène Grandmougin and Ed. Dessoulavy (*Ber.*, 1909, **42**, 4401—4407. Compare Abstr., 1909, i, 968).—*Indigotindianilide hydrochloride*, prepared by the interaction of indigotindianilide in acetic acid with alcoholic hydrogen chloride, forms dark bluish-green needles. The corresponding *sulphate* is very similar.

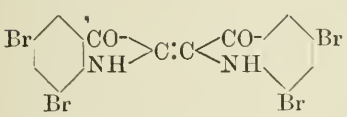
Dehydroindigotindianilide nitrate is prepared by adding four times its weight of 50% nitric acid to indigotindianilide, which immediately changes its blue colour to a brilliant red. The nitrate crystallises in rosettes of red needles; the alcoholic solution is turned violet by alcoholic potassium hydroxide, but on heating it turns a dirty green and indigotindianilide separates. To obtain the corresponding base, the nitrate is suspended in pyridine and oxidised with lead peroxide, whereby a brownish-red, crystalline substance is obtained, which yields red salts with acids and is partly converted on heating into indigotindianilide. The nitrate is a tetranitrate, but part of the nitric acid is lost during drying.

Dehydroindigotindi-p-toluidide tetranitrate resembles the anilide, and gives the characteristic violet coloration with potassium hydroxide. The corresponding *tetrahydrochloride* forms a red, crystalline precipitate.

7 : 7′-Dimethylindigotindi-*p*-toluidide, prepared by heating dimethyl-

indigotin with *p*-toluidine and boric acid, crystallises in dark blue needles with a copper reflex. Chromic acid oxidises it to *o*-methylisatin, and nitric acid to the red 7 : 7′-dimethyldehydroindigotindi-*p*-toluidide tetranitrate. E. F. A.

Indigotin. III. 5 : 7 : 5′ : 7′-Tetrabromoindigotin. Eugène Grandmougin (*Ber.*, 1909, 42, 4408—4411).—Tetrabromoindigotin is best prepared by brominating indigotin with 8 atoms of bromine in boiling nitrobenzene; it crystallises in lustrous copper crystals. The solubility depends largely on the purity of the product; it forms a blue solution in concentrated sulphuric acid. On oxidation in the cold with nitric acid, 5 : 7-dibromoisatin is formed; distillation with potassium hydroxide gives rise to 2 : 4-dibromoaniline. The constitution is therefore established (annexed formula).



On successive bromination of indigotin, 5 : 5′-dibromo-, 5 : 7 : 5′-tribromo-, and 5 : 7 : 5′ : 7′-tetrabromo-derivatives are formed; on further bromination the halogen probably enters the positions 4 : 4′.

The leuco-compound of tetrabromoindigotin is readily obtained on reduction in alcoholic suspension with sodium hydrogen sulphite. This dissolves in alkalis with a yellow coloration, and dyes cotton yarn fast blue shades. E. F. A.

Preparation of Azines from Nitroso-β-naphthols and *o*-Phenylenediamine. Fritz Ullmann and Robert Heisler (*Ber.*, 1909, 42, 4263—4268).—α-Nitroso-β-naphthol, reacting as the tautomeric naphthaquinoneoxime, condenses with a boiling acetic acid solution of *o*-phenylenediamine in the presence of dilute hydrochloric acid, yielding αβ-naphthaphenazine (Witt, Abstr., 1887, 591):

$$C_{10}H_6\begin{matrix}N\cdot OH\\ O\end{matrix}\!\!>\!\!\begin{matrix}NH_2\\ NH_2\end{matrix}C_6H_4 + HCl =$$

$$C_{10}H_6\!<\!\begin{matrix}N\\ |\\ N\end{matrix}\!>\!C_6H_4 + 2H_2O + NH_2\cdot OH,HCl,$$

which can be isolated by fractional precipitation with water. It is crystalline, and has m. p. 142°. A by-product formed during the reaction is 2 : 3-diaminophenazine (Griess, *J. pr. Chem.*, 1871, [ii], 3, 142; Fischer and Hepp, Abstr., 1889, 499).

9-Hydroxynaphthaphenazine (Kehrmann and Brunnel, Abstr., 1908, i, 579) can be obtained from 7-hydroxy-β-naphthaquinoneoxime (Clausius, Abstr., 1890, 627) and *o*-phenylenediamine, or even better from the zinc salt of the nitrosonaphthol. Its *acetyl* derivative, $C_{18}H_{12}O_2N_2$, crystallises in brownish-yellow needles, m. p. 207°. The *methyl ether*, $C_{17}H_{12}ON_2$, forms glistening, yellowish-brown needles, m. p. 168°, and yields solutions with a green fluorescence.

Naphthaphenazine-5-carboxylic acid, $C_{16}N_2H_6\cdot CO_2H$, obtained from 1-nitroso-2 : 3-hydroxynaphthoic acid (Kostanecki, Abstr., 1894, i, 91) and *o*-phenylenediamine, forms yellow needles, and when heated forms αβ-naphthaphenazine. The *sodium* salt, $C_{17}H_9O_2N_2Na$, forms yellow, glistening needles. *Naphthaphenazine-8-sulphonic acid*,

$C_{16}H_{10}O_3N_2S$, obtained from 1-nitroso-2-naphthol-8-sulphonic acid (Meldola, Trans., 1880, 39, 41) and *o*-phenylenediamine, crystallises in orange-yellow needles. The *barium* salt, $Ba(C_{16}H_9O_3N_2S)_2$, forms a red precipitate.

7-Acetylamino-naphthaphenazine, $C_{16}N_2H_9{\cdot}NHAc$, from 1-nitroso-5-acetylamino-2-naphthol and *o*-phenylenediamine without the aid of hydrochloric acid, crystallises in pale yellow, felted needles, m. p. 311—313°, and when hydrolysed with sulphuric acid yields *7-amino-naphthaphenazine*, $C_{16}H_{11}N_3$, as glistening, reddish-brown needles, m. p. 270—271°. J. J. S.

Function of the Nitrogen Atoms in Primary Hydrazines. Max Busch (*Ber.*, 1909, 42, 4596—4602).—A continuation of the investigations of the author and his co-workers on the interaction of primary hydrazines with carbimides and thiocarbimides (compare Abstr., 1901, i, 234; 1903, i, 537; 1904, i, 628). It has been shown (*loc. cit.*) that βδ-dialkylthiosemicarbazides are formed by the interaction of hydrazines and thiocarbimides in cold alcohol, whereas αδ-dialkylthiosemicarbazides are produced at higher temperatures or when the components are allowed to interact in the absence of a solvent; it would appear therefore that the amine in cold alcohol is present as an ammonium base, $NHR{\cdot}NH_3{\cdot}OH$, in consequence of which it does not form a βδ-dialkylthiosemicarbazide, owing to the saturated character of the β-nitrogen atom. This view is supported by the following observations: (1) βδ-Diphenylthiosemicarbazide is formed by the interaction of phenylhydrazine and phenylthiocarbimide in alcohol, even at a high temperature, provided an acid, such as acetic or hydrochloric, is present. (2) The product of the reaction when the components are dissolved in benzene or ether, even at a low temperature, contains about 70% of αδ-diphenylthiosemicarbazide.

Phenylcarbimide behaves like its sulphur analogue, but exhibits a greater tendency to combine with the β-nitrogen atom of the hydrazine.

The course of the reaction in the case of alphylhydrazines is not altered by the presence of an acid; thus, methylhydrazine sulphate and benzylhydrazine hydrochloride react with phenylthiocarbimide in alcoholic-acetic acid solution, yielding βδ-dialkylthiosemicarbazides.

βδ-Diphenylthiosemicarbazide hydrochloride, $C_{13}H_{13}N_3S,HCl$, crystallises in small aggregates of microscopic leaflets, softens at 160°, m. p. 170° (decomp.). W. H. G.

Addition of Thiocarbimides to Ring-substituted Arylhydrazines. Max Busch and Johannes Reinhardt (*Ber.*, 1909, 42, 4602—4610).—Contrary to the statement of Marckwald (Abstr., 1897, i, 503), arylhydrazines containing substituents in the ortho-, meta-, or para-positions combine with thiocarbimides in alcoholic solution, particularly in the presence of acetic acid at a low temperature yielding βδ-dialkylthiosemicarbazides, which are fairly stable, passing into the αδ-dialkyl isomerides when fused; in a few cases the βδ-derivatives have not been isolated owing to experimental difficulties.

δ-Phenyl-β-m-tolylthiosemicarbazide, $C_{14}H_{15}N_3S$, prepared from

m-tolylhydrazine and phenylthiocarbimide, crystallises in silvery, flat needles or leaflets, m. p. 132—133°, and condenses with benzaldehyde, yielding δ-*phenyl*-β-m-*tolyl*-α-*benzylidenethiosemicarbazide*,

$$NHPh\cdot CS\cdot N(C_7H_7)\cdot N:CHPh,$$

which crystallises in small, yellow nodules, m. p. 104°. The parent substance remains unchanged when treated with an alcoholic solution of hydrochloric acid, but passes into δ-*phenyl*-α-m-*tolylthiosemicarbazide*, $C_{14}H_{15}N_3S$, glistening, white leaflets, m. p. 156—157°, when heated for a short time at 135°.

δ-o-*Tolyl*-β-m-*tolylthiosemicarbazide* crystallises in colourless leaflets, m. p. 120—121°; the *hydrochloride*, $C_{15}H_{17}N_3S,HCl$, forms white needles, m. p. 162°; δ-o-*tolyl*-α-m-*tolylthiosemicarbazide* forms granular aggregates of microscopic leaflets, m. p. 148°.

δ-p-*Tolyl*-β-m-*tolylthiosemicarbazide* forms glistening leaflets, m. p. 130—131°; the α-m-*nitrobenzylidene* derivative, $C_{22}H_{20}O_2N_4S$, crystallises in pale yellow needles or prisms, m. p. 198°; δ-p-*tolyl*-α-m-*tolylthiosemicarbazide* forms tufts of needles or rectangular prisms, m. p. 145—146°.

Methylthiocarbimide reacts with *m*-tolylhydrazine in the presence of glacial acetic acid, yielding a *substance*, crystallising in glistening, yellow prisms, m. p. 119—120°; an alcoholic solution of the components at 60° yields small quantities of a *substance*, crystallising in white prisms, m. p. 163°.

δ-*Phenyl*-β-m-*chlorophenylthiosemicarbazide* forms small, colourless, compact crystals, m. p. 117°; the α-*benzylidene* derivative,

$$C_{20}H_{16}N_3ClS,$$

crystallises in glistening, white leaflets or hexagonal plates, m. p. 146°; δ-phenyl-α-*m*-chlorophenylthiosemicarbazide has m. p. 153° (slight decomp.); Marckwald gives m. p. 138—139° (*loc. cit.*).

β-m-*Chlorophenyl*-δ-*methylthiosemicarbazide* crystallises in glistening, white needles, m. p. 105°; the α-m-*nitrobenzylidene* derivative,

$$C_{15}H_{13}O_2N_4ClS,$$

forms pale yellow needles, m. p. 224°; α-m-*chlorophenyl*-δ-*methylthiosemicarbazide* has m. p. 177°.

δ-*Phenyl*-β-m-*bromophenylthiosemicarbazide* forms colourless crystals, m. p. 130°; the *benzylidene* derivative, $C_{20}H_{16}N_3BrS$, crystallises in glistening, yellow prisms, m. p. 164°; δ-phenyl-α-*m*-bromophenylthiosemicarbazide has m. p. 159—160°; the compound described by Marckwald (*loc. cit.*), m. p. 113°, is probably a mixture of the isomerides.

α-Bromophenyl-δ-methylthiosemicarbazide has m. p. 175° (decomp.) (Illgen gives m. p. 127—128°: *Diss.*, Berlin, 1894); a *substance* crystallising in tufts of white needles, m. p. 103°, is obtained by the action of methylthiocarbimide on *m*-bromophenylhydrazine in cold alcoholic solution; it is not an α-thiosemicarbazide.

δ-*Phenyl*-β-m-*nitrophenylthiosemicarbazide* forms aggregates of flat, pale yellow needles, m. p. 133°; the *benzylidene* derivative,

$$C_{20}H_{16}O_2N_4S,$$

crystallises in pale yellow, matted needles, m. p. 165—166°.

δ-*Phenyl*-β-2-*naphthylthiosemicarbazide*, prepared by acting on β-naphthylhydrazine with phenylthiocarbimide in alcohol containing

acetic acid, crystallises in leaflets, m. p. 185°; the corresponding *δ-methyl* compound forms leaflets, m. p. 172° (decomp.); the *benzylidene* derivative of the former substance, $C_{24}H_{19}N_3S$, forms white leaflets, m. p. 206—207°.

δ-Phenyl-β-o-tolylthiosemicarbazide crystallises in glistening, white leaflets, m. p. 124°.

δ-Phenyl-β-o-anisylthiosemicarbazide forms leaflets, m. p. 140—141°; the m-*nitrobenzylidene* derivative, $C_{21}H_{18}O_3N_4S$, crystallises in small, rectangular, yellow plates, m. p. 199—200°. W. H. G.

Isatinanils. I. Isatin-dimethylamino-2-anil. Its Formation, Hydrate, and Salts. Rudolf Pummerer and Max Goettler (*Ber.*, 1909, 42, 4269—4279).—Isatin-2-anils (α-isatinanilides) can be prepared by the condensation of aromatic nitroso-derivatives with indoxylic acid in aqueous alcoholic solution. When nitrosobenzene and indoxylic acid are used, isatin-2-anil, m. p. 125—126°, is obtained.

With *p*-nitrosodimethylaniline and indoxylic acid in neutral or faintly acid solution at 15°, the chief product is a violet, crystalline powder, m. p. 105°, which yields isatin with sulphuric acid. Recrystallisation of the violet compound from 80% acetone converts it into *isatin*-p-*dimethylamino*-2-*anil*, $C_6H_4<^{NH}_{CO}>C{:}N{\cdot}C_6H_4{\cdot}NMe_2$, which crystallises in intensely coloured prisms with a green, metallic lustre. It contains $1{\cdot}5H_2O$, and has m. p. 182°. When powdered it has a green colour, but gives a red streak. When heated at 100° it loses its water of hydration and forms dichroic prisms with a metallic lustre, and then crystallises in bluish-red prisms, m. p. 182°. When the anil or its hydrate is shaken with an excess of an ethereal solution of hydrogen chloride, a yellow *dihydrochloride*,

$$C_{16}H_{15}ON_3,2HCl,$$

m. p. 135—136°, is obtained, but when an excess of hydrogen chloride is avoided, a *monohydrochloride*, $C_{16}H_{15}ON_3,HCl,0{\cdot}5H_2O$, is formed; it crystallises in brilliant blue prisms with a violet, metallic lustre, and readily absorbs water. When heated to about 120°, an isomeric yellow *monohydrochloride* is formed, and from its deep reddish-brown aqueous solution isatin is gradually precipitated. Rubbing the blue salt with chloroform or acetone also transforms it into the yellow isomeride.

The *oxalate*, $C_{16}H_{15}ON_3,1{\cdot}5H_2C_2O_4$, crystallises in blue needles, m. p. 155°. The *picrate*, $2C_{16}H_{15}ON_3,C_6H_3O_7N_3$, crystallises in bluish-black prisms, m. p. 179—180°.

When alkylated with sodium ethoxide and methyl iodide, the anil gives a *methyl* derivative, $C_{17}H_{17}ON_3$, which crystallises in lustrous, black plates, m. p. 125—126°, and yields 1-methylisatin on hydrolysis with hydrochloric acid.

Acids readily decompose *p*-dimethylamino-2-anil into isatin and *p*-aminodimethylaniline salts, which react in the presence of sodium carbonate, yielding *isatin*-p-*dimethylamino*-3-*anil*, $C_{16}H_{15}ON_3$, m. p. 221—222°.

Violet-coloured dyes are formed when nitroso-compounds are condensed with indoxylic acid in alkaline solution. J. J. S.

Preparation of 1-*p*-Dialkylaminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolones. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 214716).—The 1-*p*-dialkylaminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolones are of therapeutic interest as being remarkably powerful antipyretics; they are produced by alkylating 1-*p*-aminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone with methyl iodide or methyl sulphate, the former methylation taking place in alcoholic solution. 1-p-*Dimethylaminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone* is a colourless, crystalline substance melting at 212—213°. 1-p-*Aminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone*, colourless prisms, m. p. 249°, is produced by reducing 1-p-*nitrophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolene*, yellow crystals, m. p. 178—179°, the latter being obtained by condensing *p*-nitrophenylhydrazine and methyl acetoacetate to 1-*p*-nitrophenyl-3 : 4-dimethyl-5-pyrazolone, methylating this compound to 1-p-*nitrophenyl*-2 : 3 : 4-*trimethyl*-5-*pyrazolone*, yellow needles, m. p. 132°, brominating to 1-p-*nitrophenyl*-2 : 4-*dimethyl*-3-*bromomethyl*-5-*pyrazolone*, m. p. 213—214°, then treating this substance with alkali acetate in glacial acetic acid, whereby the bromine is replaced by hydroxyl, yielding 1-p-*nitrophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone acetate*, yellow crystals, m. p. 163—164°, which, on hydrolysis with dilute sulphuric acid, gives the nitro-alcohol.

F. M. G. M.

Preparation of Xanthine and Guanine Derivatives containing Substituents in Position 8. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 213711).—The *o*-diaminopyrimidines, $Y{:}C\langle^{NX\text{———}CO}_{NX{\cdot}C(NH_2)}\rangle C{\cdot}NH_2$, yield formyl, acetyl, and propionyl derivatives, which, when heated, undergo further condensation to furnish xanthine and guanine compounds. This reaction has been generalised, with the result that the following acids can be employed for the condensation: oxalic, succinic, cyanoacetic, glycollic, lactic, hydantoic, *a*-hydroxy*iso*butyric, hippuric, acetylglycollic, ethoxy- and methoxy-acetic, and *aβ*-dihydroxypropionic acids.

4-*Amino*-5-*oxalylamino*-2 : 6-*dioxy*-3-*methylpyrimidine*,

$$CO\langle^{NH\text{———}CO}_{NMe{\cdot}C(NH_2)}\rangle C{\cdot}NH{\cdot}CO{\cdot}CO_2H,$$

is obtained by condensing, at 160—170°, 4 : 5-diamino-2 : 6-dioxy-3-methylpyrimidine and fused oxalic acid; it crystallises with $1H_2O$, and gives a *disodium* salt, which, on heating at 150—160°, yields the sodium salt of 3-*methylxanthine*-8-*carboxylic acid*,

$$\begin{matrix} NH\text{—}CO{\cdot}C{\cdot}NH \\ | \quad\quad\quad\quad \| \\ CO{\cdot}NMe{\cdot}C\text{—}N \end{matrix}\rangle C{\cdot}CO_2H,$$

the free acid of which crystallises with $1\frac{1}{2}H_2O$, and at 160° gives rise to 3-*methylxanthine*.

4-*Amino*-5-*cyanoacetylamino*-2 : 6-*dioxy*-1 : 3-*dimethylpyrimidine*,

$$CO\langle^{NMe{\cdot}CO\text{———}}_{NMe{\cdot}C(NH_2)}\rangle C{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN,$$

acicular crystals, is obtained by heating, at 120—130°, 4 : 5-diamino-2 : 6-dioxy-1 : 3-dimethylpyrimidine with cyanoacetic acid.

Theophylline-8-acetic acid, $\begin{matrix}\mathrm{NMe\cdot CO\cdot C\cdot NH}\\ \mathrm{CO\cdot NMe\cdot C{-}\!\!-N}\end{matrix}\!\!>\!\mathrm{C\cdot CH_2\cdot CO_2H}$, is produced by heating the foregoing compound with aqueous sodium hydroxide until ammonia is completely evolved; it separates from water in aggregates of white needles.

Ethyl theophylline-8-acetate, prepared by passing hydrogen chloride into the foregoing compound suspended in alcohol, forms crystals, melting at 215°.

2 : 4-*Diamino-5-succinylamino-6-pyrimidone*,

$$\mathrm{NH_2\cdot C<\begin{matrix}\mathrm{N:C(OH)}\\ \mathrm{N\cdot C(NH_2)}\end{matrix}\!\!>C\cdot NH\cdot CO\cdot C_2H_4\cdot CO_2H},$$

prepared from 2 : 4 : 5-triamino-6-pyrimidone and succinic acid, gives rise to *succinylguaninepropionic* acid and the *hydrochloride* of *ethyl guaninepropionate*, $\mathrm{HCl,NH_2\cdot C<\begin{matrix}\mathrm{N:C(OH)\cdot C\cdot NH}\\ \mathrm{N\text{———}C{-}\!\!-N}\end{matrix}\!\!>C\cdot C_2H_4\cdot CO_2Et}$.

4-*Amino-5-cyanoacetylamino-2 : 6-dioxy-3-methylpyrimidine*,

$$\mathrm{CO<\begin{matrix}\mathrm{NH\text{———}CO}\\ \mathrm{NMe\cdot C(NH_2)}\end{matrix}\!\!>C\cdot CO\cdot CH_2\cdot CN},$$

prepared from 4 : 5-*diamino-2 : 6-dioxy-3-methylpyrimidine* and cyanoacetic acid, furnishes 3-*methylxanthine-8-acetic acid* on heating with excess of aqueous sodium hydroxide. The *compound*,

$$\mathrm{CO<\begin{matrix}\mathrm{NMe\cdot CO\cdot C\cdot NH}\\ \mathrm{NMe\text{——}C{-}\!\!-N}\end{matrix}\!\!>CH_2\cdot OH},$$

m. p. 240°, is obtained by heating 4 : 5-diamino-2 : 6-dioxy-1 : 3-dimethylpyrimidine and hydroxyacetic acid, and then warming the first condensation product with concentrated aqueous barium hydroxide.

The patent contains examples of several other condensation products of similar type containing lactyl, succinyl, and aceturyl groups.

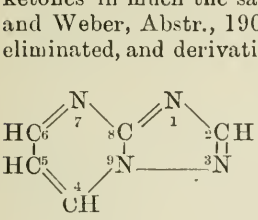
F. M. G. M.

Hydrazo-compounds. IV. Reactions of Hydrazobenzene with Aliphatic Aldehydes and with Benzoyl Chloride. Berthold Rassow and Otto Baumann (*J. pr. Chem.*, 1909, [ii], 80, 511—518).—The investigations of Rassow and Lummerzheim (Abstr., 1901, i, 777) have been extended to other aldehydes.

1 : 2 : 4 : 5-*Tetraphenyl-3 : 6-dihexylhexahydro-1 : 2 : 4 : 5-tetrazine*, $\mathrm{C_6H_{13}\cdot CH<\begin{matrix}\mathrm{NPh\cdot NPh}\\ \mathrm{NPh\cdot NPh}\end{matrix}\!\!>CH\cdot C_6H_{13}}$, m. p. 133°, is obtained by adding heptaldehyde to a hot solution of hydrazobenzene in 90% alcohol. Equal molecular quantities of hydrazobenzene and propaldehyde react with development of heat to form mainly *propylidenebishydrazobenzene*, NHPh·NPh·CHEt·NPh·NHPh, m. p. 152°. The minor product of the reaction, 3 : 6-*diethylhexahydro-1 : 2 : 4 : 5-tetrazine*, m. p. 193°, becomes the sole product when the aldehyde is added to hot 90% alcoholic hydrazobenzene.

Benzoylhydrazobenzene, NPhBz·NHPh, m. p. 136°, is obtained in 80% yield when an ethereal solution of hydrazobenzene and benzoyl chloride (2 mols.) is boiled with magnesium oxide; a second benzoyl group cannot be introduced. C. S.

Synthetical Experiments on the Preparation of Derivatives of Hetero-condensed-heterocyclic "1 : 3-Triazo-7 : 0'-pyrimidine" [1 : 3 : 7 : 9-Benztetrazole]. Carl Bülow and Karl Haas (*Ber.*, 1909, 42, 4638—4644).—5-Amino-1 : 3 : 4-triazole (Thiele and Manchot, Abstr., 1899, i, 168) condenses with 1 : 3-diketones in much the same manner as 1-amino-1 : 3 : 4-triazole (Bülow and Weber, Abstr., 1909, i, 614, 615); two molecules of water are eliminated, and derivatives of "1 : 3-triazo-7 : 0'-pyrimidine" [1 : 3 : 7 : 9-benztetrazole] (annexed formula) are formed.



When the 5-aminotriazole is condensed with ethyl acetoacetate and its homologues, 6- or 5 : 6-substituted derivatives of 4-hydroxy-1 : 3 : 7 : 9-benztetrazole (heterohydroxylic acids) are obtained. The presence of the hydroxylic group imparts strongly acidic properties to the compounds, so that they yield neutral sodium salts, and can be titrated readily by means of standard alkali.

4 : 6-*Dimethyl*-1 : 3 : 7 : 9-*benztetrazole*, $\begin{matrix}CMe{=}N\cdot C{:}N\\ CH{:}CMe\cdot N\cdot N\end{matrix}\!\!>\!CH$, obtained by boiling an alcoholic solution of 5-amino-1 : 3 : 4-triazole with acetylacetone and a few drops of piperidine for fifteen hours, crystallises in colourless needles, m. p. 133°. It is readily volatile, it forms an unstable compound with nitric acid, and with silver nitrate an additive compound, $C_7H_8N_4,AgNO_3$, which crystallises in short, stout needles.

4 : 5 : 6-*Trimethyl*-1 : 3 : 7 : 9-*benztetrazole*, $C_8H_{10}N_4$, obtained in a similar manner from methylacetylacetone, crystallises in colourless needles, m. p. 135—136°.

Benzoylacetone condenses slowly with 5-amino-1 : 3 : 4-triazole in glacial acetic acid solution, yielding tarry matter and 6-*phenyl*-4-*methyl*-1 : 3 : 7 : 9-*benztetrazole*, $C_{12}H_{10}N_4$, which crystallises in needles, m. p. 134°.

4-*Hydroxy*-6-*methyl*-1 : 3 : 7 : 9-*benztetrazole*, $\begin{matrix}CMe{=}N{-}{-}C{:}N\\ CH{:}C(OH)\cdot N\cdot N\end{matrix}\!\!>\!CH$, obtained by boiling for two hours a glacial acetic acid solution of 5-amino-1 : 3 : 4-triazole with ethyl acetoacetate, crystallises in colourless, glistening needles, m. p. 271° after sintering at 261°. A solution of the potassium salt gives amorphous precipitates with solutions of silver and copper salts. The *mercuric*, *lead*, *zinc*, *barium*, *calcium*, and *cobalt* salts have been obtained in crystalline forms.

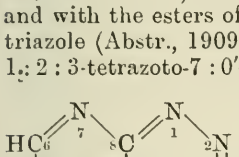
4-*Hydroxy*-6-*methyl*-5-*ethyl*-1 : 3 : 7 : 9-*benztetrazole*, $C_8H_{10}ON_4$, obtained from ethyl ethylacetoacetate and 5-methyl-1 : 3 : 4-triazole, crystallises in felted needles, m. p. 268° after sintering at 250°. Crystalline *copper*, *cadmium*, *manganese*, *calcium*, and *magnesium* salts have been prepared.

When a glacial acetic acid solution of ethyl diacetylsuccinate is boiled for four hours with the 5-aminotriazole, *ethyl* 1-(2' : 4' : 5'-)*triazolyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,

$$\begin{matrix}CH\cdot N\\ N{-}{-}N\end{matrix}\!\!>\!C\cdot N\!<\!\begin{matrix}CMe{:}C\cdot CO_2Et\\ CMe{:}C\cdot CO_2Et\end{matrix}$$

(compare Abstr., 1906, i, 906), is obtained. It crystallises from benzene and has m. p. 113°. J. J. S.

Hetero-condensed, Heterocyclic Compounds with Two Nuclei: Substituted "Tetrazotopyrimidines." Carl Bülow (*Ber.*, 1909, 42, 4429—4438).—*C*-Aminotetrazotic acid reacts with 1 : 3-diketones and with the esters of 1 : 3-ketocarboxylic acids similarly to 1-aminotriazole (Abstr., 1909, i, 614, 615), with production of derivatives of 1,: 2 : 3-tetrazoto-7 : 0′-pyrimidine [1 : 2 : 3 : 7 : 9-benzpentazole] (annexed formula). Condensation of aminotetrazotic acid with acetylacetone yields 4 : 6-*dimethyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, which crystallises in long needles and has m. p. 150°. From methylacetylacetone, 4 : 5 : 6-*trimethyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, m. p. 123—123·5°, is obtained; it also crystallises in needles. 5-*Phenyl*-6-*methyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, prepared from benzoylacetone, forms white needles, m. p. 185°.



C-Aminotetrazotic acid condenses with ethyl acetoacetate, forming 4-*hydroxy*-6-*methyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, which crystallises in needles, and has m. p. 246—247°; it yields crystalline, *mercurous*, *mercuric*, *lead*, *barium*, *iron*, and *strontium* derivatives. 4-*Hydroxy*-6-*phenyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, prepared from ethyl benzoylacetate, forms white needles, m. p. 261° (decomp.). Both these compounds are strongly acidic, and may be titrated sharply with phenolphthalein; they are therefore to be regarded as heterohydroxylic acids (Abstr., 1909, i, 615).

By diazotising *C*-aminotetrazotic acid (Thiele, Abstr., 1892, 1299) and treating the product with acetoacetic ester, the azo-compound, *ethyl tetrazolylazoacetoacetate*, $\begin{matrix}N---N\\ \|\\ N\cdot NH\end{matrix}\!\!>\!C\cdot N{:}N\cdot CHAc\cdot CO_2Et$, is obtained; it forms yellow needles, m. p. 140—141°. The *phenylhydrazone* has m. p. 192—193°; on continued boiling with glacial acetic acid, it is converted into 4-*tetrazolylazo*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, which has m. p. 201° (decomp.), and is apparently dimorphous (orange-yellow needles and deep red, compact crystals). R. V. S.

Preparation of a Soluble Double Compound of Theophylline and Piperazine. Chemische Werke vorm. Dr. Heinrich Byk (D.R.-P. 214376).—*Piperazine-theophylline* is formed by combining molecular proportions of its components; it has an alkaline reaction, and is readily soluble in water, more sparingly so in alcohol.

F. M. G. M.

The Gelatinisation of Egg-Albumin by Hydrochloric Acid. I. Giovanni Moruzzi (*Biochem. Zeitsch.*, 1909, 22, 232—243).—The electrical conductivities and depression of freezing points of mixtures of egg-white solution and hydrochloric acid of concentrations $N=0$ to $N\times 0{\cdot}692$ were determined, and compared with these physical constants for the same strengths in the absence of proteins. The degree of gelatinisation was noted in each case in the mixtures of

protein with acid. The maximum of $\Delta - \Delta'$ was noted when the normality of the acid reached 0·055, and remained about constant until the normality 0·554 was reached. In higher concentrations the value $\Delta - \Delta'$ was negative. The gelatinisation occurred between the concentration 0·103 and 0·244*N*. Experiments were also made to determine the changes of the viscosity of the mixtures during the process of gelatinisation, when the strength of acid = 0·018*N*. The electrical resistance and depression of freezing point remained constant during the time in which the viscosity increased. The change produced is apparently therefore neither molecular nor ionic, but probably due to a hydration of the colloid. S. B. S.

The Hexone Bases from White of Egg. H. G. Chapman and J. M. Petrie (*J. Physiol.*, 1909, 39, 341—345).—By complete hydrolysis of 100 grams of egg-white with 25% sulphuric acid, the yield of hexone bases was as follows: arginine, 2·39; histidine, 0·66, and lysine, 3·19 grams. W. D. H.

The Caseinogen-Peptones containing Phosphorus. M. Dietrich (*Biochem. Zeitsch.*, 1909, 22, 120—130).—The products investigated were made by the peptic digestion of caseinogen, and isolated by Reh's method by means of precipitation by uranium salts. They were converted into calcium salts, which were separated into two fractions, one of which was insoluble on heating, and the other soluble. The former was dissolved in water, acidified with acetic acid, the solution neutralised, and from the solution thus obtained, other fractions were separated by means of copper, zinc, and lead salts. The fractions differed from one another in their readiness to yield inorganic phosphorus on hydrolysis. From the fractions of calcium salt which did not separate on heating, a peptone was separated by precipitation with uranyl acetate. The uranium precipitate was decomposed by hydroferrocyanic acid. The nitrogen and phosphorus were estimated in the various fractions. The caseinphosphoric acid isolated by means of the zinc salt was obtained in the largest quantity. It yielded, on hydrolysis, lysine, proline, and glutamic acid. S. B. S.

Synthesis through Ferment Action. Alonzo E. Taylor (*Zeitsch. physikal. Chem.*, 1909, 69, 585—597. Compare Abstr., 1909, ii, 344).—General remarks on the reversibility of enzyme reactions. G. S.

Action of Proteolytic Enzymes on Protamines. M. Takemura (*Zeitsch. physiol. Chem.*, 1909, 63, 201—214).—The following enzymes were found capable of acting on protamines in a weakly acid medium. Hedin's lieno-β-protease, Hahn and Geret's endotryptase, and papain. The action of pepsin is slight, and probably due to admixture with β-proteases. W. D. H.

Reversibility of Enzyme Actions and the Effect of External Factors on Enzymes (Invertase, Maltase). Friedrich G. Kohl (*Bied. Zentr.*, 1909, 38, 718; from *Beiheft Bot. Centr.*, 1908,

23, i, 646—640).—Yeast extracts which were found to contain the largest amounts of invertase were allowed to act, in absence of light, on sucrose solutions of known strength at fixed temperatures, after excluding bacterial infection by means of thymol or chloroform. It was found that the dextrose and lævulose increased for some time, after which the amounts generally remained stationary or the enzyme action was reversed. The time depended on the concentration and the temperature. Diffused daylight retards inversion, and 0·05% of asparagine quickens the hydrolysis. N. H. J. M.

Hydrolysis of Salicin by the Enzyme Emulsin. C. S. Hudson and H. S. Paine (*J. Amer. Chem. Soc.*, 1909, 31, 1242—1249).—The hydrolysis of salicin by strong acids has been shown by Noyes and Hall (Abstr., 1896, ii, 159) to follow the law of unimolecular reactions. It has been stated by Henri, however, that the hydrolysis of the glucoside by emulsin does not take place in accordance with this law, and that the dextrose produced has $[\alpha]_D$ 52°.

Experiments have now been carried out which have given the following results. The dextrose formed by the action of emulsin on salicin is β-dextrose, $[\alpha]_D$ 20°. During the hydrolysis, the readings of the polarimeter are affected by the mutarotation of the dextrose, and this constituted a source of error in Henri's determinations. Measurements of the true rate of hydrolysis of salicin by emulsin at 0° and 30° have been made by rendering the solution slightly alkaline before determining its rotatory power. The results show that the rate follows the unimolecular order. Emulsin is only active in a nearly neutral solution, the activity being completely destroyed by sodium hydroxide of 0·005N and by hydrochloric acid of 0·014N concentration. E. G.

Influence of Acids on the Loss of Activity of Rennet Caused by Shaking. Signe Schmidt-Nielsen and Sigval Schmidt-Nielsen (*Zeitsch. physikal. Chem.*, 1909, 69, 547—556).—When a glycerol extract of rennet, diluted with water, is vigorously shaken in a tube, it rapidly loses its activity. The effect does not depend on the dissolving of alkali from glass, as it is also observed in quartz tubes.

In the quantitative experiments, the rennet solution was contained in a tube of Jena glass, and agitated by the up-and-down motion of an ebonite stirrer. The diminution of activity with the time of shaking does not follow any simple law; the rate of the diminution increases rapidly as the temperature is raised, but becomes less as the enzyme concentration is increased.

Acids, even in great dilution, lessen the rate of diminution of activity very considerably. Hydrochloric acid is most efficient in this respect; lactic, oxalic, and tartaric acids are about equally efficient, and acetic acid is least effective. The behaviour of sulphuric acid is remarkable, inasmuch as above a certain concentration further addition of acid has no action.

Commercial preparations of rennet are not affected by shaking, probably because they contain acids and neutral salts. G. S.

Chemical Composition and Biological Function of an Oxydase. Hans Euler and Ivar Bolin (*Zeitsch. physikal. Chem.*, 1909, 69, 187—202).—The preparation of an oxydase from *Medicago sativa* is described. The fresh plants were comminuted, the juice pressed out, treated with alcohol, the precipitate redissolved, again precipitated by alcohol, and this process repeated several times. The product, in the form of a white powder, very soluble in water, was again dissolved in water, the solution boiled and filtered to remove proteins, the filtrate treated with charcoal, again filtered, precipitated with three times its volume of 96% alcohol, and the resulting powder dried in a vacuum. The preliminary treatment of the juice with alcohol may be omitted. The product, which showed all the properties of an oxydase, proved on analysis to consist of the neutral salts (mainly calcium salts) of certain polybasic organic acids, among which glycollic, mesoxalic, citric, malic, and probably glyoxylic acids have been detected. The acids were partly separated by fractional crystallisation of their barium salts.

Experiments on the accelerating influence of "laccase" and of salts of organic hydroxy-acids on the oxidation of polyphenols by free oxygen in the presence of manganese salts have already been described (compare Abstr., 1908, ii, 1021), and these experiments have now been extended. The rate of absorption of oxygen increases less rapidly than the manganese concentration, and also less rapidly than the concentration of the neutral salt of the oxyacid employed. The neutral salts of the different acids differ somewhat in catalytic power, but the effect is independent of the nature of the cation.

The physiological action of the oxydases is discussed. They do not effect the direct oxidation of sugars or fats. Sugar is partly broken down under the influence of enzymes, and the simpler compounds thus formed then undergo oxidation. G. S.

Preparation of Derivatives of Phenylarsenious Oxide and of Arsenobenzene. Farbwerke vorm Meister, Lucius and Brüning (D.R.-P. 212205. Compare Abstr., 1908, i, 591; 1909, i, 347).—*2-Aminotolyl-5-arsenious oxide*, $NH_2 \cdot C_6H_3Me \cdot AsO$, a white, crystalline powder, m. p. 160°, is prepared by reducing 4-amino-3-tolylarsinic acid in sulphuric acid solution by means of sulphurous acid in presence of potassium iodide.

Acetylaminocarboxyphenylarsenious oxide, $NHAc \cdot C_6H_3(AsO) \cdot CO_2H$, a colourless powder, is prepared by boiling 2-acetylaminotolyl-5-arsinic acid during two hours with phenylhydrazine in methyl-alcoholic solution.

o-Tolylglycine-5-arsinic acid, $CO_2H \cdot CH_2 \cdot NH \cdot C_6H_3Me \cdot AsO(OH)_2$, m. p. 220° (decomp.), is prepared by treating 2-aminotolyl-5-arsinic acid with chloroacetic acid, and on reduction with sodium hyposulphite at 50° yields *p-arseno-o-tolylglycine*, a yellowish-brown powder, which blackens when heated above 200°. *Arsenoacetylanthranilic acid*, a bright yellow powder, is prepared by reducing 2-acetylaminotolyl-5-arsinic acid with sodium hyposulphite in the presence of sodium acetate. F. M. G. M.

Organic Chemistry.

Cuprous Compounds of Ethylene and of Carbon Monoxide. Wilhelm Manchot and W. Brandt (*Annalen*, 1909, **370**, 286—296).—Manchot and Friend have shown (Abstr., 1908, ii, 375) that the combination of cuprous chloride with carbon monoxide depends on the formation of a compound, $CuCl,CO,2H_2O$, or analogous substances containing ammonia, aniline, toluidine, etc., in place of water. It is now found that cuprous chloride and ethylene likewise combine, forming a dissociative compound in which one mol. of ethylene is united with 1CuCl; the combination takes place, however, only in the presence of water, aniline, etc.; cuprous chloride does not form an additive product with dry ethylene, neither do these substances interact when dissolved in absolute alcohol.

All attempts to isolate the additive compound, which is far more soluble in water than cuprous chloride, have been unsuccessful, owing to the readiness with which it dissociates. Under identical conditions the ethylene compound is dissociated, as a general rule, to a far greater degree than the analogous carbon monoxide compound.

As in the case of the compounds of ferrous salts with nitric oxide (compare Manchot and Zechentmayer, Abstr., 1907, ii, 93), so also with the additive products of cuprous chloride with carbon monoxide and ethylene: when the concentration of the gas is kept constant the degree of dissociation is increased by raising the temperature.

W. H. G.

Specific Gravity of Solutions of Alcohols: Mixtures of Propyl Alcohol with Water. Antony G. Doroschewsky and M. S. Roschdestvensky (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1428—1438).—The authors first discuss the literature concerning the specific gravity of propyl alcohol and its aqueous solutions. Their own experiments on the carefully purified and dehydrated alcohol give the value D_{15}^{15} 0·80804 and the conductivity $0·089 \times 10^{-6}$ at 15°, these numbers not being altered by further distillation of the alcohol over calcium. The specific gravities of aqueous solutions containing from 0 to 100% of the alcohol were determined, the results being tabulated; the contractions for the various mixtures have been calculated.

T. H. P.

Stereochemical Isomerides of Δγ-Hexin-βε-diol. Georges Dupont (*Compt. rend.*, 1909, **149**, 1381—1383).—*Δγ-Hexin-βε-diol*, OH·CHMe·C:C·CHMe·OH, has been described by Iotsitch (*Journ. Russ. Phys. Chem. Soc.*, 1903, **35**, 430). When this compound is treated with bromine in chloroform solution, it yields a *dibromide*, m. p. 214—215°, mentioned by Iotsitch. The liquid from which this crystallises contains an isomeric *dibromide*, $C_6H_{10}O_2Br_2$, m. p. 119—120°. When treated with zinc dust and alcohol, these derivatives

give two isomeric glycols: Iotsitch's compound, yielding crystals, m. p. 69—70°, b. p. 122°/15 mm., D_{13} 1·0205, n_D^{13} 1·4698, and forming a *diacetyl* derivative, m. p. 36°. The second glycol is a viscous liquid, b. p. 121°/15 mm., D_{13} 1·023, n_D 1·4733; the *diacetyl* derivative has m. p. 23—24°. Both glycols regenerate the corresponding dibromide when treated with bromine.

It follows, therefore, that the glycol prepared by Iotsitch is a mixture of these two isomerides. W. O. W.

Oxidation of Unsaturated Compounds with Organic Superoxides. Nikolaus Prileschaéeff (*Ber.*, 1909, **42**, 4811—4815. Compare Gambarjan, Abstr., 1909, i, 910).—Oxidation was carried out with benzoylhydroperoxide ($C_6H_5\cdot CO\cdot O\cdot OH$) dissolved in a neutral solvent at 0°, to which the calculated quantity of the unsaturated compound was added. The temperature is not allowed to rise above ordinary room temperature. The following oxides have been characterised.

Octylene oxide has b. p. 157—158°/740 mm., D_0^0 0·8395, D_{15}^{15} 0·8272, n_D^{15} 1·4165. On hydration, a glycol, b. p. 135—136°/20 mm., is obtained.

Diisobutylene oxide has b. p. 138—139°/765·5 mm, D_0^0 0·8418, D_{16}^{16} 0·8290, n_D^{16} 1·4157. It yields two glycols: *methylisoamylethylene glycol*, m. p. 60—61°, and *dimethyl*-tert.-*butylethylene glycol*, m. p. 64·5—65°.

Decylene oxide has b. p. 116—117°/50 mm., D_0^0 0 8465, D_{16}^{16} 0·8337, n_D^{16} 1·4275. The corresponding *glycol* has b. p. 151—152°/14 mm.

Propylene oxide, b. p. 162—163°/751 mm., D_0^0 1·1270, D_{16}^{16} 1·1136, n_D^{16} 1·4350. It does not yield glycerol on hydration, but forms a *hydroxychloroacetate*, b. p. 125—127°/17 mm.

Geraniol oxide has b. p. 157—158°/25 mm., D_0^0 0·9716, D_{16}^{16} 0·961, n_D^{16} 1·4681. A *triol*, b. p. 205—207°/20 mm., is formed on hydration.

Geraniol dioxide, formed when 2 mols. of benzoyl hydroperoxide are employed, has b. p. 180—183°/25 mm., D_0^0 1·0587, D_{16}^{16} 10472, n_D^{16} 1·4653. On hydration, a *trioloxide*, b. p. 220°/15 mm., m. p. 137—138°, is formed.

Linalool oxide has b. p. 95°/25 mm., D_0^0 0·9660, D_{16}^{16} 0·9507, $[\alpha]_D$ −4·98°, n_D^{16} 1·4554. It yields a doubly unsaturated *aldehyde* when hydrated, b. p. 120—122°/25 mm., D_0^0 0·8706, D_{16}^{16} 0·8573, n_D^{16} 1·5038, of which the *semicarbazone* has b. p. 138·5°.

Linalool dioxide has b. p. 131—133°/25 mm., D_0^0 1·0552, D_{16}^{16} 1·0423, $[\alpha]_D$ +5·34°, n_D^{16} 1·4616. It forms a *trioloxide*, b. p. 210—212°/25 mm., when hydrated.

Citral oxide has b. p. 146—148°/20 mm., D_0^0 1·0091, D_{16}^{16} 0·9740, n_D^{16} 1·4604, and gives a *diolaldehyde*, b. p. 141—142°/24 mm., D_0^0 1·0584, D_{16}^{16} 1·0335, when hydrated.

Citronellal oxide has b. p. 130—131°/25 mm., D_0^0 0·9437, D_{16}^{16} 0·9344, n_D^{16} 1·4421. On hydration, a *diolaldehyde*, b. p. 180—182°/18 mm., is formed.

Limonene oxide has b. p. 113—114°/50 mm., D_0^0 0·9435, D_{16}^{16} 0 9303, $[\alpha]_D$ −6·76°, n_D^{16} 1·4693, and yields a *glycol*, m. p. 66·5—67·5°.

Limonene dioxide has b. p. 146·5—147°/50 mm., D_0^0 1·0471,

D_{16}^{16} 1·0338, $[\alpha]_D$ +52·23°, n_D^{16} 1·4702. It forms an amorphous erythritol on oxidation, b. p. above 220°/23 mm.

Pinene oxide has b. p. 102—103°/50 mm., D_0^0 0·9812, D_{16}^{16} 0·9689, $[\alpha]_D$ −92°, n_D^{16} 1·4708; it is readily hydrated, forming sobrerol, m. p. 150°.

Aniline and 1 mol. of benzoylhydroperoxide form azobenzene; with 2 mols., nitrosobenzene is formed. In each case, a little nitrobenzene is formed. *o*-Toluidine gives *o*-nitrotoluene. E. F. A.

Results of Heating the Chlorides of the Higher Fatty Acids. Augustin Bistrzycki and August Landtwing (*Ber.*, 1909, 42, 4720—4723).—The chlorides of the higher primary fatty acids do not lose carbon monoxide when heated (compare Abstr., 1908, i, 270), but it is now shown that they lose hydrogen chloride. Palmityl chloride, when heated at 250—275° for four hours in a current of dry carbon dioxide, gives an almost theoretical yield of hydrogen chloride. From the residue a small amount of a product, *tris-tetradecylketen*, $(C_{16}H_{30}O)_3$, has been isolated, which crystallises from alcohol in plates. It softens at 60°, is completely molten at 72°, and is analogous to the compounds obtained by Wedekind and Hacussermann (Abstr., 1908, i, 671) by the action of tertiary amines on acyl chlorides.

Lauryl chloride, under similar conditions, yields a *product*, $C_{12}H_{22}O$, m. p. 49—58°, and nonyl chloride, a solid product.

J. J. S.

α-Ethylpentenoic Acids and Xeronic Anhydride. Fritz Fichter and Hans Obladen (*Ber.*, 1909, 42, 4703—4707. Compare Fichter and Mueller, Abstr., 1906, i, 622).—*γ-Methyl-α-ethylparaconic acid*, $CO<\begin{matrix}O\text{——}CHMe\\ |\\ CHEt\cdot CH\cdot CO_2H\end{matrix}$, obtained by reducing α-ethylacetylsuccinic ester with sodium amalgam and alcohol, has b. p. 192—196°/12 mm., and crystallises from a mixture of ether and light petroleum in colourless needles, m. p. 111°. When distilled slowly under atmospheric pressure, it yields unaltered acid, xeronic anhydride (Fittig, *Annalen*, 1887, 188, 59), and *α-ethyl-Δ$^{\beta}$-pentenoic acid*, $CHMe{:}CH\cdot CHEt\cdot CO_2H$. The latter forms a gummy *barium* salt, has b. p. 116°/12 mm., and when boiled with 20% sodium hydroxide solution yields a mixture of α-ethyl-Δ$^{\alpha}$-pentenoic acid and unaltered Δ$^{\beta}$-acid, the latter of which can be removed as *α-ethylvalerolactone* by treatment with 62% sulphuric acid (Young, Abstr., 1883, 455).

The Δ$^{\alpha}$-unsaturated acid has b. p. 120°/12 mm., and its *barium* salt, $(C_7H_{11}O_2)_2Ba,H_2O$, crystallises in slender needles.

γ-Methyl-α ethylitaconic acid, $CHMe{:}C(CO_2H)\cdot CHEt\cdot CO_2H$, is formed when xeronic anhydride, $O<\begin{matrix}CO\cdot CEt\\ ||\\ CO\cdot CEt\end{matrix}$, is boiled with 20% sodium hydroxide solution for twenty-four hours. The acid forms slender crystals, m. p. 136°, and yields an *anhydride*, $C_8H_{10}O_3$, as an oil, b. p. 142—144°/12 mm.

Xeronic anhydride and *p*-toluidine yield *xeronic*-p-*tolil*, needles, m. p. 107°. The isomeric *γ-methyl-α-ethylitacon*-p-*tolil* has m. p. 88° and b. p. 220°/12 mm. J. J. S.

β-Methylpentenoic Acids. Fritz Fichter and Erwin Gisiger (*Ber.*, 1909, **42**, 4707—4710).—A comparison of the dissociation constants of β-methyl-Δ^{α}-pentenoic acid and β-methyl-Δ^{β}-pentenoic acid shows that the Δ^{β}-unsaturated acid is the stronger acid; the values for K are Δ^{α}-acid, 0·00073, and Δ^{β}-acid, 0·00255 (compare Abstr., 1904, i, 965; 1906, i, 622). The Δ^{β}-acid was prepared by reducing α-methylacetylsuccinic ester (Bischoff, Abstr., 1881, 412) with sodium and aqueous alcohol to βγ-dimethylparaconic acid, and distilling the latter slowly under atmospheric pressure. It was not found possible to isolate the isomeric Δ^{α}-acid from the mixture of acids obtained by boiling the Δ^{β}-acid with 10% sodium hydroxide solution, as both acids are converted by 62% sulphuric acid into β-methylvalerolactone (compare following abstract). The Δ^{α}-acid was therefore prepared by the elimination of hydrogen bromide from α-bromo-β-methyl-β-ethylpropionic acid.

βγ-Dimethylparaconic acid, $CO<\begin{matrix}CH_2\cdot CMe\cdot CO_2H\\ O\text{---}CHMe\end{matrix}$ (50% yield), has b. p. 196°/9 mm., and crystallises in plates, m. p. 80°. The *ethyl* ester has b. p. 134°/10 mm. *β-Methyl-Δ^{β}-pentenoic acid*, $CHMe{:}CMe\cdot CH_2\cdot CO_2H$, has b. p. 96°/10 mm., or 199° under atmospheric pressure.

Ethyl α-bromo-β-methyl-n-*valerate*, $CH_2Me\cdot CHMe\cdot CHBr\cdot CO_2Et$, obtained by brominating β-methylvaleric acid (Bentley, Trans., 1895, **67**, 264) by Auwers and Bernhardi's method (Abstr., 1891, 1189), using a Hirsch shaking apparatus, and subsequent treatment of the product with ethyl alcohol, has b. p. 91°/12 mm. When heated with quinoline, hydrogen bromide is eliminated and *ethyl β-methyl-Δ^{α}-pentenoate*, $CH_2Me\cdot CMe{:}CH\cdot CO_2Et$, b. p. 176°, is formed. The corresponding *acid*, $C_6H_{10}O_2$, has m. p. 46° and b. p. 104°/12 mm., or 207° under atmospheric pressure. The *calcium* salt, $(C_6H_9O_2)_2Ca,H_2O$, crystallises in brilliant plates, and the *zinc* salt, which also contains $1H_2O$, in needles.

The formation of the isomeric Δ^{β}-unsaturated acid by the removal of hydrogen bromide from the brominated ester was not observed (compare Rupe, Ronus, and Lotz, Abstr., 1903, i, 139). J. J. S.

Remarkable Transformation of β-Dialkylated Acrylic Acids when Boiled with Sulphuric Acid. Fritz Fichter, Albert Kiefer, and Walter Bernoulli (*Ber.*, 1909, **42**, 4710—4713).—Fittig's statement (Abstr., 1894, i, 204) that Δ^{β}-unsaturated acids are transformed into the isomeric lactones when heated with 62% sulphuric acid, whereas the Δ^{α}-unsaturated acids are unaffected, is not without exceptions (compare Blaise and Luttringer, Abstr., 1905, i. 168). It is shown that β-methyl-Δ^{α}-pentenoic acid (preceding abstract) is quantitatively transformed into β-methylvalerolactone when heated with 62% sulphuric acid. Under similar conditions, β-ethyl-Δ^{α}-pentenoic acid yields β-ethylvalerolactone.

Ethyl iso*pentylmalonate*, $CHEt_2\cdot CH(CO_2Et)_2$, obtained from γ-iodopentane and sodioethylmalonate, has b. p. 130°/16 mm. The *acid*, $C_8H_{14}O_4$, has m. p. 58°, and yields a *sodium hydrogen* salt,

$$C_8H_{13}O_4Na,9H_2O,$$

in the form of colourless plates. *β-Ethyl*-n-*valeric acid*,

$$CHEt_2\cdot CH_2\cdot CO_2H,$$

has b. p. 212°. *Ethyl α-bromo-β-ethyl*-n-*valerate*, $CHEt_2\cdot CHBr\cdot CO_2Et$, has b. p. 165°/25 mm., and with quinoline yields *ethyl β-ethyl-*Δ^{α}*-pentenoate*, $CEt_2{:}CH\cdot CO_2Et$, which has b. p. 187—188°. The *acid*, $C_8H_{13}O_2Br$, has b. p. 217—218°, and the *toluidide*, $C_{14}H_{19}ON$, has m. p. 95° and b. p. 210—215°/15 mm. J. J. S.

Decomposition of Crotonic Acid by Heating with Ammonia. Fritz Fichter and Hans P. Labhardt (*Ber.*, 1909, **42**, 4714—4715. Compare Engel, Abstr., 1888, 1063).—When crotonic acid is heated with the compound $CaCl_2,8NH_3$ for eight to ten hours at 225—230°, the chief product is 2-methyl-5-ethylpyridine (Auerbach, Abstr., 1893, i, 175). The formation of this compound is to be attributed to the decomposition of the crotonic acid into acetaldehyde and acetic acid, and the condensation of the former to aldehydecollidine.

[With Albert Kiefer.]—Dimethylacrylic acid under similar conditions yields *s*-trimethylpyridine. J. J. S.

Synthesis of β-Hydroxy-α-*iso*propylbutyric Acid. I. Matzurevitsch (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1319—1324).—The action of zinc on a mixture of acetaldehyde and ethyl α-bromo-β-methylbutyrate (α-bromo*iso*valerate) proceeds according to the equations: (1) $CHMe_2\cdot CHBr\cdot CO_2Et + Zn = CHMe_2\cdot CH(ZnBr)\cdot CO_2Et$; (2) $CHMe_2\cdot CH(ZnBr)\cdot CO_2Et + CH_3\cdot CHO =$ $ZnBr\cdot O\cdot CHMe\cdot CH(CHMe_2)\cdot CO_2Et$, and the latter $+ H_2O = OH\cdot CHMe\cdot CHPr^{\beta}\cdot CO_2Et + ZnBr\cdot OH$.

*Ethyl β-hydroxy-α-*iso*propylbutyrate*, $OH\cdot CHMe\cdot CHPr^{\beta}\cdot CO_2Et$, best prepared in presence of benzene, is a yellow, mobile liquid with a faint, pleasant odour, b. p. 111·5—114°/38—37 mm., D_4^{30} 0·97182, n_D^{30} 1·43296; it gives the normal molecular weight in boiling ether. The corresponding *acid* was obtained as an almost colourless liquid; the *sodium*, *potassium*, and *barium* salts were prepared and analysed. T. H. P.

Ketens. XIV. Ethyl Ethylketencarboxylate. Hermann Staudinger and St. Bereza (*Ber.*, 1909, **42**, 4908—4918. Compare this vol., i, 46).—An ethereal solution of ethyl bromoethylmalonate chloride reacts with zinc, producing ethyl ethylketencarboxylate,

$$CO{:}CEt\cdot CO_2Et,$$

which rapidly polymerises, forming, with 80% yield, 1 : 3-*diethyl*cyclo*butan*-2 : 4-*dione*-1 : 3-*dicarboxylate*, $CO_2Et\cdot CEt\langle{}^{CO}_{CO}\rangle CEt\cdot CO_2Et$, which distils in a high vacuum at 113—116° as a colourless oil. With aniline it yields ethyl ethylmalonanilate. When heated in an oil-bath at 180—200°, it is depolymerised, and the unimolecular keten passes over. *Ethyl ethylketencarboxylate* so prepared is a colour-

less liquid, b. p. 48°/15 mm., m. p. 57·86°. It has the characteristic properties, not of a ketoketen, but of an aldoketen. It is probable that all ketens form bimolecular polymerides, which are *cyclo*butane derivatives. The bimolecular polymeride of keten itself is probably not an acetylketen (compare Chick and Wilsmore, Trans., 1908, **93**, 946), but Δ^1-cyclo*buten*-1-*ol*-3-*one*, $CO<\begin{matrix}CH_2\\CH\end{matrix}>C\cdot OH$.

Ethyl ethylmalonate chloride, obtained from the ester-acid by means of phosphorus pentachloride, has b. p. 75—77°/13 mm. It yields an *anilide*, m. p. 55—56°. *Ethyl α-bromoethylmalonate chloride*, prepared from the above chloride by the action of bromine in hot carbon disulphide solution, has b. p. 95—102°/14 mm. R. V. S.

Action of Ethyl Bromoacetate and Zinc on the Anhydrides of Monobasic Acids. Andreas Luniak (*Ber.*, 1909, **42**, 4808—4811). —By the interaction of molecular quantities of ethyl bromoacetate and acid anhydrides, *C*-diacyl compounds are obtained. Thus acetic anhydride yielded ethyl-α-acetylacetoacetate, isolated as the copper salt, m. p. 149°. From propionic anhydride the *copper* salt of *ethyl dipropionylacetate* was obtained, crystallising in dark violet crystals, which turned greyish-green at 84° (corr.), m. p. 98° to a dark green liquid. *Ethyl dipropionylacetate* is a colourless liquid of characteristic odour, b. p. 120·5—121·5°/20 mm., D_4^{20} 1·0527. The *copper* salt of *ethyl dibutyrylacetate* forms a bright violet precipitate of thin prisms; it becomes greyish-green at 89° (corr.), m. p. 98°. *Ethyl dibutyrylacetate* is a colourless liquid, b. p. 139—140°/24 mm., D_4^{20} 1·0168, and shows a dark red coloration with ferric chloride. *Ethyl* O-*butyrylbutyrylacetate* (*β-butyryloxy-Δ*$^{\alpha}$*-hexenoate*),

$$CH_2Me\cdot CH_2\cdot C(O\cdot CO\cdot C_3H_7):CH\cdot CO_2Et,$$

has a characteristic fruity odour, b. p. 137—137·5°/12 mm., D_4^{20} 0·9956, and shows no ferric chloride coloration. E. F. A.

Action of Magnesium *tert.*-Butyl Chloride on Ethyl Oxalate. Mlle. V. I. Egorova (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1454—1468). —In syntheses of alcohols by means of organo-magnesium compounds, just as in syntheses effected with organo-zinc derivatives, the reactions may proceed in two directions, according to the conditions. One of these conditions is the temperature, the raising of which promotes reduction, and another, which is not possessed by aromatic radicles, the more or less marked reducing properties of the radicle combined with the magnesium (compare Bouveault, Abstr., 1904, i, 546; Sabatier and Mailhe, Abstr., 1905, i, 706; Letellier, Abstr., 1908, i, 242). With ethyl oxalate and magnesium *tert.*-butyl chloride, as was to be expected, the reaction follows an abnormal course, owing to the pronounced reducing properties of the Grignard compound. In order that both the ethoxy-groups of the ethyl oxalate may react, to 1 mol. of the oxalate must be taken 4 mols. of magnesium *tert.*-butyl chloride, 2 mols. for the introduction of the radicles, and two for forming the 2 mols. of magnesium hydrogen chloride necessary for the reduction.

The reaction gives rise to the following products: (1) *iso*butylene;

(2) α-hydroxy-ββ-dimethylbutyric acid, $CMe_3 \cdot CH(OH) \cdot CO_2H$, which forms rectangular plates, m. p. 87—88°; (3) *α-ethoxy-ββ-dimethylbutyric acid*, $CMe_3 \cdot CH(OEt) \cdot CO_2H$, m. p. 121°, the *calcium* salt of which is more soluble in cold than in hot water; (4) the ethyl ester of another acid, formed only in small quantity; (5) the *ketone*, $CMe_3 \cdot CO \cdot CH_2 \cdot CMe_3$, which is a colourless liquid, b. p. 152·5—154·5°, with a camphor-like odour, and is probably formed by the dehydration, by the alcoholic potassium hydroxide employed for hydrolysis, of part of (6) the *glycol*, $CMe_3 \cdot CH(OH) \cdot CH(OH) \cdot CMe_3$, m. p. 90—92°, b. p. 120—130°/33 mm., which has a camphor-like odour; (7) hexamethylethane.

The formation of these various products is explained by the following scheme:

(1) $CO_2Et \cdot CO_2Et + CMe_3 \cdot MgCl = CMe_3 \cdot C(OEt)(OMgCl) \cdot CO_2Et$; (2) $CMe_3 \cdot MgCl = CH_2 \cdot CMe_2 + MgHCl$; (3) $CMe_3 \cdot C(OEt)(OMgCl) \cdot CO_2Et + MgHCl$ gives either $CMe_3 \cdot CH(OMgCl) \cdot CO_2Et \longrightarrow CMe_3 \cdot CH(OH) \cdot CO_2Et \longrightarrow CMe_3 \cdot CH(OH) \cdot CO_2H$ or $CMe_3 \cdot CH(OEt) \cdot CO_2Et \longrightarrow CMe_3 \cdot CH(OEt) \cdot CO_2H$. When, on the other hand, 2 mols. of the organo-magnesium compound take part in the reaction, the latter proceeds as follows: (1) $CO_2Et \cdot CO_2Et + 2CMe_3 \cdot MgCl = CMe_3 \cdot C(OEt)(OMgCl) \cdot C(OEt)(OMgCl) \cdot CMe_3$, and (2) this + $2MgHCl \longrightarrow CMe_3 \cdot CH(OMgCl) \cdot CH(OMgCl) \cdot CMe_3 \longrightarrow CMe_3 \cdot CH(OH) \cdot CH(OH) \cdot CMe_3$; (3) $CMe_3 \cdot CH(OH) \cdot CH(OH) \cdot CMe_3 - H_2O = CMe_3 \cdot CO \cdot CH_2 \cdot CMe_3$, and (4) $CMe_3 \cdot MgCl + CMe_3Cl = CMe_3 \cdot CMe_3 + MgCl_2$.

T. H. P.

Production of Traces of Formaldehyde in the Oxidation of Ethyl Alcohol by Chemical, Physical, or Biological Methods. E. Voisenet (*Compt. rend.*, 1910, **150**, 40—43).—Advantage has been taken of the coloration developed by formaldehyde in a solution of albumin containing nitrous acid, to test for this substance in the products of oxidation of pure alcohol (Abstr., 1906, ii, 59). Definite proof of the presence of formaldehyde was obtained whether the oxidation was effected by the chromic acid mixture, by electrolysis, by contact with finely divided metals, or through the agency of micro-organisms. W. O. W.

A New Cupric Salt and its Application as a Fungicide for Diseases of the Vine and Other Plants. Philippe Malvezin (*Bull. Soc. chim.*, 1909, [iv], **5**, 1096—1098).—When cupric hydroxide, or copper hydrogen carbonate, is suspended in a 40% aqueous solution of formaldehyde, and sulphur dioxide is passed through the mixture, a deep blue solution is formed. This contains the substance represented by the formula: $Cu(SO_3 \cdot CH_2 \cdot OH)_2$, which it is proposed to call cupric diformaldisulphite. The following is suggested as the method of formation of this product: $CH_2O \longrightarrow CH_2(OH)_2 \longrightarrow OH \cdot CH_2 \cdot O \cdot SO_2H \longrightarrow Cu(SO_3 \cdot CH_2 \cdot OH)_2$. The advantages in practice of this substance as a fungicide over "Bordeaux mixture" and other cupric products are described. T. A. H.

Catalytic Hydrogenation of Unsaturated Organic Compounds. H. Fournier (*Bull. Soc. chim.*, 1910, [iv], **7**, 23—27).—The substance to be reduced is placed in a flask containing platinum-black, and communicating with a supply of hydrogen. Sometimes it is advantageous to dissolve the substance in ether. The mixture is kept continuously agitated, and the action continued until hydrogen is no longer absorbed. The catalytic activity of the platinum may be restored when necessary by heating the metal for a few minutes at 200—220°.

Under these conditions crotonaldehyde furnishes *n*-butyraldehyde and *n*-butyl alcohol, *iso*safrole and safrole give dihydrosafrole, and eugenol and *iso*eugenol yield dihydroeugenol [propylguaiacol] (compare Delange, *Bull. Soc. chim.*, 1908, [iv], **3**, 505, and Parrain, Abstr., 1907, i, 43). T. A. H.

Conversion of *iso*Butyl Alcohol into α-Methylglyceraldehyde. Simon Zeisel and M. Danieк (*Monatsh.*, 1909, **30**, 727—728. Compare Viguier, Abstr., 1909, i, 691).—*iso*Butyl alcohol was converted into *iso*butaldehyde, and this by means of bromine in presence of marble transformed into the *methylacetal* of *α-bromoisobutaldehyde*. Potassium hydroxide at high temperatures converted this into the *methylacetal* of α-methylacraldehyde, from which, by means of potassium permanganate, α-methylglyceraldehyde methylacetal was obtained and converted into the free aldehyde. E. F. A.

Preparation and Description of Condensation Products of Sodium Derivatives of the Acyloins (Hydroxyketones) with Esters of the Acetic Series. Louis Bouveault and René Locquin (*Bull. Soc. chim.*, 1909, [iv], **5**, 1136—1144).—An extension of a paper already published (Abstr., 1907, i, 479), giving details of the methods of preparation used, descriptions of compounds prepared by the general reaction, and in some cases additional data regarding substances described already. It is now proposed to represent the condensation products of this reaction by the following typical formula :

$$\begin{matrix} CH_2R\cdot CH\cdot CH_2 \\ | \\ CHR{:}C\text{-----}O \end{matrix}\!\!>\!CO,$$

whilst the esters from them are to be represented by that formerly proposed (*loc. cit.*) :

$$\begin{matrix} CH_2R\cdot CH \\ | \\ CH_2R\cdot C \end{matrix}\!\!=\!\!>\!C\cdot CO_2Me.$$

The reasons for the adoption of these formulæ are as follows. The condensation products are (1) only feebly acid, (2) form dibromides, and (3) are readily attacked by oxidising agents, giving 1 mol. each of a fatty acid and a substituted succinic anhydride, (4) the esters formed from them are reduced by sodium in alcohol to homologues of *cyclo*propanecarbinol, so that they must contain a trimethylene ring and a double linking in the *αβ*-position with respect to the carboxyl group.

The condensation products were prepared as already described (*loc. cit.*). They gave small yields of esters when esterified by the usual methods, and recourse was therefore had to the use of

diazomethane for this purpose. In this way yields of about 80% of the theoretical were obtained.

The product $\begin{matrix}CHEt\cdot CH\cdot CH_2\\ CHMe{:}C\text{------}O\end{matrix}>CO$, b. p. 190—195°/12 mm., obtained from propioin, is liquid at the ordinary temperature, and cannot be obtained crystalline (*loc. cit.*).

The corresponding *substance*, $C_{10}H_{16}O_2$, b. p. 210—215°/20 mm., m. p. 116°, obtained from butyroin, crystallises from boiling water ; it furnishes an *amide*, m. p. 63—64°, and yields an *ethyl* ester, $C_{12}H_{20}O_2$, b. p. 160°/18 mm. (approx.), and a *methyl* ester, b. p. 143—148°/10 mm. The latter on reduction furnishes *dipropylcyclopropanecarbinol*, b. p. 96—98°/8 mm. or 104—105°/12 mm., which has a mint-like odour, and yields an *acetate* having the same boiling point as itself, and a *pyruvate*, b. p. 125°/8 mm. (approx.), of which the *semicarbazone* has m. p. 97—98°.

*iso*Butyroin under the same conditions yields a *product*, $C_{10}H_{16}O_2$, b. p. 200—210°/25 mm., which crystallises in part.

Hexonoin yields a substance, $C_{14}H_{24}O_2$, b. p. 250—260°/20 mm. and m. p. 100—111° (*loc. cit.*), which on keeping decomposes spontaneously, yielding valeric acid and a second acid, possibly amylsuccinic acid. The methyl ester from this condensation product has b. p. 205°/19 mm. (*loc. cit.*). T. A. H.

Effect of Negative Substituents on the Formation of Semicarbazones. Hans Rupe and Sidonius Kessler (*Ber.*, 1909, **42**, 4715—4720. Compare this vol., i, 15).—The influence of negative groupings (Rupe and Metz, Abstr., 1903, i, 535) on semicarbazone formation is shown in the following reactions. β-Bromo*iso*butyl methyl ketone, $CMe_2Br\cdot CH_2\cdot COMe$, forms a semicarbazone readily, mesityl oxide dibromide, $CMe_2Br\cdot CHBr\cdot COMe$, with difficulty, and bromomesityl oxide, $CMe_2{:}CBr\cdot COMe$, does not form a semicarbazone.

Aliphatic oximino-ketones react with semicarbazide, yielding semicarbazones, and with excess of the carbazide the oximino-group is eliminated and bis-semicarbazones are formed. Oximino-derivatives of the aromatic series react but slowly with semicarbazide, or, in some cases, do not react at all.

Methyl β-bromoisobutyl ketone, $C_6H_{11}OBr$, obtained by the addition of hydrogen bromide to mesityl oxide, is a clear, colourless oil, b. p. 52—53°/11 mm., and when kept, even in the absence of air, forms a dark-coloured syrup. The *semicarbazone*,

$$CMe_2Br\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

crystallises in slender, colourless needles, m. p. 113° (decomp.).

Mesityl oxide dibromide (Claisen, this Journ., 1876, i, 985), obtained by passing a current of carbon dioxide saturated with bromine vapour into mesityl oxide cooled with ether and solid carbon dioxide, yields a *semicarbazone*, $C_7H_{13}ON_3Br_2$, which crystallises in pale yellow, glistening needles, m. p. 290—295°.

Oximinoacetone-semicarbazone, $OH\cdot N{:}CH\cdot CMe{:}N\cdot HN\cdot CO\cdot NH_2$, forms small, colourless, pointed needles, m. p. 218° (decomp.), and yields an *acetyl* derivative, $C_6H_{10}O_3N_4$.

Oximinomethyl propyl ketone-semicarbazone,

$$OH\cdot N{:}CEt\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

forms a crystalline powder, m. p. 228°, and yields an *acetyl* derivative, $C_8H_{14}O_3N_4$, m. p. 207°.

Pyruvaldehydebis-semicarbazone, $C_5H_{10}O_2N_6$, obtained by the action of an excess of semicarbazide hydrochloride on oximinoacetone, crystallises in slender, lustreless needles, m. p. 254—255° (decomp.).

Acetylpropionylbis-semicarbazone,

$$NH_2\cdot CO\cdot NH\cdot N{:}CMe\cdot CEt{:}N\cdot NH\cdot CO\cdot NH_2,$$

obtained from oximinomethyl propyl ketone, has m. p. 250°.

Oximinobenzylideneacetone reacts in the course of several weeks with an aqueous alcoholic solution of semicarbazide, yielding a small amount of a *semicarbazone*,

$$CHPh{:}CH\cdot C(:N\cdot NH\cdot CO\cdot NH_2)\cdot CH{:}N\cdot OH,$$

m. p. 197° (decomp.).

A bis-semicarbazone could not be obtained. J. J. S.

Electrolysis of Dextrose, Glycerol, and Glycol. Walther Löb [in part with G. Pulvermacher] (*Zeitsch. Elektrochem.*, 1910, **16**, 1—9).—A solution containing from 20 to 60% of dextrose and 5% of sulphuric acid was placed in a porous pot containing a spiral of lead tubing, which was cooled with water and served as anode. The current density was about 0·05 ampere per sq. cm., and the temperature about 16°. The electrolysis was stopped when a comparatively small quantity of the dextrose was oxidised. The changes which occur are interpreted thus: dextrose is first hydrolysed to arabinose and formaldehyde. Dextrose itself is oxidised to gluconic and saccharic acids, arabinose to arabonic and trihydroxyglutaric acids, and formaldehyde to formic acid and carbon monoxide and dioxide. The non-volatile acids were not identified with certainty, as they were separated in the form of a mixture of their calcium salts. When the lead coil is used as cathode instead of anode, the greater part of the dextrose is reduced to mannitol, but formaldehyde and a pentose (yielding an osazone, m. p. 170—172°), were also present in small quantities.

l-Arabinose, when oxidised in the same way as dextrose, yields formaldehyde and a sugar, from which a tetrose has not yet been isolated.

Glycerol yields considerable quantities of formaldehyde and a pentose (probably *i*-arabinose). It is probable that glyceraldehyde is the first product of the oxidation; this is hydrolysed into glycolaldehyde and formaldehyde, and the glycolaldehyde and glyceraldehyde then condense to a pentose. Formic acid is the only volatile acid present, and the non-volatile acids are probably tartronic and trihydroxyglutaric acids, formed by oxidation of glycerol and the pentose respectively. The oxidation of ethylene glycol, under the conditions used for the other substances, yields formaldehyde, formic acid, and carbon dioxide, and minute quantities of a sugar and a non-volatile acid which is not glycollic acid. The sugar was not a pentose, and contained neither dihydroxyacetone, glyceraldehyde, nor glycolaldehyde. It gave an osazone melting at 184—185°, and was probably a hexose. T. E.

The Scission of Sugars. VII. The Reversal of the Sugar Synthesis. Walther Löb and Georg Pulvermacher (*Biochem. Zeitsch.*, 1909, 23, 10—26).—The authors have investigated the action of lead hydroxide and sodium hydroxide on sugar solutions under varying conditions. They have isolated formaldehyde, pentose, acetylcarbinol, acetylmethylcarbinol, formic acid, polyhydroxy-acids, and possibly pentitol. Their main conclusions are: the sugar synthesis is a reversible one; formaldehyde and pentose are phases in sugar scission and sugar synthesis; the scission of dextrose into formaldehyde and pentose takes place in solutions, the alkalinity of which corresponds with that of the blood; the reaction also takes place in acid solutions when, owing to oxidation or reduction, the original equilibrium has been disturbed; as shown by the electrolysis of ethylene glycol and glycerol, a sugar synthesis also takes place in acid solutions, from the aldehydes which are then formed by the scission of the sugars. S. B. S.

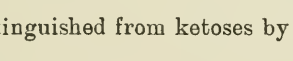
Kinetic Studies in the Sugar Series. Emil Votoček and H. Němeček (*Zeitsch. Zuckerind. Böhm.*, 1910, 34, 237—248; *Sitzungsber. böhm. Akad. Wissens.*, 1908).—The rate of action of bromine-water on the aldoses is considerably influenced by their configuration; galactose, for example, is much more rapidly oxidised than dextrose. Lævulose is not acted on by bromine water of low concentration.

The oxidation of aldoses by bromine water is retarded by hydrochloric, hydrobromic, and sulphuric acids.

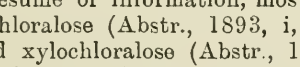
Dextrose and galactose are both oxidised at the ordinary temperature, being converted quantitatively into gluconic and galactonic acids, and it is probable that the other aldehydic sugars behave in a similar manner.

Aldoses can be distinguished from ketoses by means of the reaction with bromine water. N. H. J. M.

Choraloses. Maurice Hanriot (*Ann. Chim. Phys.*, 1909, [viii], 18, 466—502). A résumé of information, most of which has been published already: chloralose (Abstr., 1893, i, 247; 1894, i, 105); arabinochloralose and xylochloralose (Abstr., 1895, i, 321); galactochloralose and lævulochloralose (Abstr., 1896, i, 519); chloralic acids (Abstr., 1909, i, 206, 287) (compare also Heffter, Abstr., 1889, 845, and Petit and Polonowsky, Abstr., 1894, i, 394). *Mannochloralose*, m. p. 208°, yields an *acetyl* derivative, m. p. 163°, crystallising in large, colourless needles, and a *benzoyl* derivative, m. p. 152°. Mannochloralic lactone, $C_8H_7O_6Cl_3$, is best represented by the formula:



For lævulochloralose the following formula is proposed:



Dibenzoylarabinochloralose has b. p. 275°. Arabinobromalose, prepared like the chloral compound, has m. p. 210°, and occurs in small, indefinite crystals.

The chloralic acids from β-chloralose and xylochloralose are identical, and the crystals are monoclinic [$a:b:c = 1{\cdot}500:1:2{\cdot}628$; $\gamma = 83°$]. Similarly, the chloralic acids from galactochloralose and arabinochloralose are identical (the crystals are rhombic: $a:b:c = 1{\cdot}319:1:0{\cdot}825$). Mannochloralic acid is not isomeric with the other acids of this group. A discussion of isomerism among the chloraloses and their derivatives is given. T. A. H.

The Contraction Occurring when Sucrose is Dissolved in Water. G. Fouquet (*Bull. Assoc. chim. Sucr. Dist.*, 1909, **27**, 545—549. Compare Abstr., 1908, i, 855).—In reply to statements that contraction does not take place when sucrose is dissolved in water, the author points out that the values determined indirectly for the contraction depend on the density of the sugar dissolved, sucrose having been found to have the two values D 1·5881 and D 1·61. The contraction occurring when a concentrated sugar solution is diluted may be observed by placing about 200 c.c. of the solution in a 500 c.c. flask, and adding water at the same temperature up to the mark, taking care that the two mix as little as possible. On now mixing the water with the sugar solution by rotating the flask, a marked contraction of the total volume will be noticed. The author also shows that in dilute solutions the contraction is approximately proportional to the concentration. W. P. S.

Iron Double Salts of Organic Bases. Max Scholtz (*Arch. Pharm.*, 1909, **247**, 534—541).—The chlorides of almost all of the metals except iron have been frequently utilised in preparing double chlorides for the characterisation of organic bases. The ferrichlorides are very soluble in water, but are precipitated by concentrated hydrochloric acid as well crystallised compounds of constant composition. The solution of the organic base in the least possible quantity of dilute hydrochloric acid is treated with an excess of ferric chloride, and the mixture is treated slowly with fuming hydrochloric acid until it becomes turbid; after a short time, the crystalline ferrichloride separates. In the case of many aromatic amines, the method is inapplicable, since the hydrochloride of the amine is less soluble than the ferrichloride, and is therefore precipitated first.

The following new ferrichlorides are mentioned (compare Abstr., 1908, i, 202): *diethylamine ferrichloride*, $NHEt_2,HFeCl_4$, m. p. 128°, greenish-yellow prisms; *triethylamine ferrichloride*, $NEt_3,HFeCl_4$, hygroscopic, greenish-yellow needles; *tetraethylammonium ferrichloride*, $(NEt_4)FeCl_4$, groups of light yellow needles, sintering above 240°; *methyltripropylammonium ferrichloride*, $(NMePr_3)FeCl_4$, m. p. 80°, yellow, rhombic crystals; *tributylamine ferrichloride*,

$$N(C_4H_9)_3,HFeCl_4,$$

m. p. 171°, yellow needles; *amylamine ferrichloride*,

$$C_5H_{11}\cdot NH_2,HFeCl_4,$$

yellow needles; *diamylamine ferrichloride*, $NH(C_5H_{11})_2,HFeCl_4$, sinters and melts above 170°, yellow, crystalline powder; *triamylamine ferrichloride*, $N(C_5H_{11})_3,HFeCl_4$, yellow needles; *dibenzylamine ferrichloride*, $NH(C_7H_7)_2,HFeCl_4$, m. p. 145°, yellow prisms; *methylpyridinium*

ferrichloride, $C_5H_5NMe,FeCl_4$, yellow needles; *piperidine ferrichloride*, $C_5NH_{11},HFeCl_4$, m. p. 163°, yellow prisms; *benzylethylconinium ferrichloride*, like the iodide (Abstr., 1904, i, 1044), exists in two forms: the α-form has m. p. 92° and forms yellow needles; the β-form has m. p. 116° and crystallises in compact octahedra; *dibenzylconinium ferrichloride*, $C_8H_{16}N(C_7H_7)_2FeCl_4$, has m. p. 141°; *tetrahydroquinoline ferrichloride*, $C_9NH_{11},HFeCl_4$, m. p. 144°, orange-red, rhombic crystals. The additive compound of tropine and benzyl chloride (Abstr., 1905, i, 79) forms a *ferrichloride*, $C_8H_{15}ON,C_7H_7Cl,FeCl_3$, m. p. 109°, orange-yellow needles. Sparteine hydrochloride forms a *compound*,

$$C_{15}H_{26}N_2,2HCl,FeCl_3,$$

which sinters at 190°, and gradually decomposes. Sparteine methochloride forms the *compound*, $C_{15}H_{26}N_2,MeCl,HCl,FeCl_3$, yellow needles, decomposing above 240°. *o*-Xylylenedipyridinium chloride forms a *compound*, $C_6H_4(CH_2Cl,C_5NH_5,FeCl_3)_2$, m. p. 102°, yellow needles. The additive compound of *o*-xylylene bromide and triethylamine is converted by silver chloride into the chloride, which yields with ferric chloride and hydrochloric acid the *compound*,

$$C_6H_4(CH_2Cl,NEt_3,FeCl_3)_2,$$

m. p. 80°, slender, yellow needles. C. S.

Hexahalogen-irideates. [Iridichlorides and Iridibromides.] Alexander Gutbier and M. Riess (*Ber.*, 1909, **42**, 4770—4777). —On adding a solution of a substituted ammonium bromide drop by drop to a solution of hydrogen iridichloride in dilute hydrochloric acid at the ordinary temperature, a precipitate of the corresponding substituted ammonium iridichloride is formed. If, however, the solution of hydrogen iridichloride is heated to boiling while the bromide is added, some hydrobromic acid being also present, it changes colour from a reddish-brown, through green, to a deep blue. The formation of the latter colour indicates the change from the iridichloride into the iridibromide. This change can also be brought about by digesting the iridichlorides with dilute hydrobromic acid. The crystals which separate on cooling are not pure, and must be recrystallised from a dilute solution of hydrobromic acid containing free bromine.

The following compounds are described: *Methylammonium iridichloride*, $(NH_3Me)_2IrCl_6$, brownish-red needles. *Dimethylammonium iridichloride*, $(NH_2Me_2)_2IrCl_6$, reddish-brown, rhombic crystals. *Trimethylammonium iridichloride*, $(NHMe_3)_2IrCl_6$, small needles. *Ethylammonium iridichloride*, $(NH_3Et)_2IrCl_6$, brownish-red plates. *Diethylammonium iridichloride*, $(NH_2Et_2)_2IrCl_6$, brownish-red needles. *Triethylammonium iridichloride*, $(NHEt_3)_2IrCl_6$, small needles, which were not obtained pure. n-*Propylammonium iridichloride*, $(NH_3Pr^{\alpha})_2IrCl_6$, brownish-red needles. iso-*Propylammonium iridichloride*, $(NH_3Pr^{\beta})_2IrCl_6$, brownish-red needles. n-*Butylammonium iridichloride*, $(NH_3C_4H_9)_2IrCl_6$, reddish-brown plates. iso-*Butylammonium iridichloride*, $(NH_3C_4H_9)_2IrCl_6$,

brownish-red needles. *Ethylenediammonium iridichloride*, $(C_2H_{10}N_2)IrCl_6$, brownish-red needles. *Propylenediammonium iridichloride*, $(C_3H_{12}N_2)IrCl_6$, reddish-brown crystals. *Pyridinium iridichloride*, $(PyH)_2IrCl_6$, reddish-brown needles. *α-Picolinium iridichloride*, $(C_5NH_5Me)_2IrCl_6$, brownish-red needles. *Quinolinium iridichloride*, $(C_9NH_8)_2IrCl_6$, black, monoclinic prisms, or brownish-red needles. *Benzylammonium iridichloride*, $(C_7H_7\cdot NH_3)_2IrCl_6$, dark brownish-red plates.

Methylammonium iridibromide, $(NH_3Me)_2IrBr_6$, dark blue octahedra. *Dimethylammonium iridibromide*, $(NH_2Me_2)_2IrBr_6$, dark blue needles. *Trimethylammonium iridibromide*, $(NHMe_3)_2IrBr_6$, dark blue needles. *Ethylammonium iridibromide*, $(NH_3Et)_2IrBr_6$, dark blue plates. *Diethylammonium iridibromide*, $(NH_2Et_2)_2IrBr_6$, dark blue, monoclinic prisms. *Triethylammonium iridibromide*, $(NHEt_3)_2IrBr_6$, dark blue plates. n-*Propylammonium iridibromide*, $(NH_3Pr^{\alpha})_2IrBr_6$, dark blue, six-sided plates. iso*Propylammonium iridibromide*, $(NH_3Pr^{\beta})_2IrBr_6$, dark blue needles. n-*Butylammonium iridibromide*, $(NH_3\cdot C_4H_9)_2IrBr_6$, dark blue, six-sided plates. iso*Butylammonium iridibromide*, $(NH_3\cdot C_4H_9)_2IrBr_6$, dark blue plates. *Ethylenediammonium iridibromide*, $(C_2H_{10}N_2)IrBr_6$, deep blue, cubical crystals. *Propylenediammonium iridibromide*, $(C_3H_{12}N_2)IrBr_6$, deep blue prisms. *Pyridinium iridibromide*, $(PyH)_2IrBr_6$, deep blue plates. *α-Picolinium iridibromide*, $(C_5NH_5Me)_2IrBr_6$, dark blue, six-sided, monoclinic plates. *Quinolinium iridibromide*, $(C_9NH_8)_2IrBr_6$, dark blue needles. *Benzylammonium iridibromide*, $(NH_3\cdot C_7H_7)_2IrBr_6$, dark blue, six-sided plates.

The substituted ammonium iridibromides are not so stable as the alkali iridibromides, and will not withstand prolonged exposure to light. In general, the bromo-salts of the platinum metals are very readily decomposed, both as such, and in solution. T. S. P.

Behaviour of Triethylamine towards Oxidising Agents. T. Dar Juan (*Amer. Chem. J.*, 1910, **43**, 1—6).—The oxidation of triethylamine may take place either by the direct union of oxygen to form the oxide, $Et_3N{:}O$, and the subsequent oxidation of this compound to nitric and acetic acids, or by the conversion of the ethylidene groups into acetaldehyde, and the formation of ammonia. In accordance with Nef's view, the latter reaction would take place thus:

$$(C_2H_5)_3N \rightleftharpoons C_2H_4 + NH(C_2H_5)_2 \rightleftharpoons 2C_2H_4 + NH_2\cdot C_2H_5 \rightleftharpoons 3C_2H_4 + NH_3.$$

Experiments have shown that when triethylamine is oxidised with aqueous solution of potassium permanganate, the carbon residues are converted quantitatively into acetic acid, neither carbonic nor oxalic acid being produced, whilst the nitrogen appears partly as ammonia and partly as nitric acid.

In presence of potassium hydroxide, acetic acid is the chief oxidation product, but oxalic and carbonic acids are also produced. Nitric acid and ammonia are both formed, but the latter is produced in much larger quantity in this case than in the absence of alkali hydroxide. E. G.

Methylated Guanidines. Martin Schenck (*Arch. Pharm.*, 1909, **247**, 466—490).—Numerous attempts to prepare methylated guanidines by the interaction of guanidine and methyl iodide in methyl alcohol have given unsatisfactory results; the reaction does not proceed to any extent, and usually gives complicated mixtures. However, methylguanidine, $NH:C(NH_2)\cdot NHMe$, and *s*-dimethylguanidine have been isolated as the platinichlorides.

Methyl sulphate and dry guanidine sulphate do not react at the ordinary temperature, or on the water-bath, but at 150—160° the reaction leads to the formation of *s*-dimethylguanidine and a *trimethylguanidine* (*aurichloride*, m. p. 155—156°; *platinichloride*, m. p. 225—226°), which is shown to be the symmetrical compound, $NMe:C(NHMe)_2$, by comparison with a sample obtained by the interaction of *s*-dimethylthiocarbamide, excess of 10% alcoholic methylamine, and mercuric oxide on the water-bath.

The interaction of methyl iodide and the silver derivative of guanidine (prepared by Thiele's method, and also by that of Kutscher and Otori) in methyl alcohol on the water-bath is again unsatisfactory; methylguanidine and *s*-dimethylguanidine have been isolated as the platinichlorides, but the products are mainly mixtures. The author finds that the silver derivative of guanidine, prepared by the methods mentioned, always shows a deficiency of silver.

The methylguanidines obtained by the oxidation of creatine, or of methylglycocyamidine, by the interaction of methylamine and cyanamide, and those isolated from meat extract and urine are all one and the same substance, $NH:C(NH_2)\cdot NHMe$ (*aurichloride*, m. p. 198—200°, yellow needles; *platinichloride*, m. p. 194—195°, orange-red plates). C. S.

Some Guanidine Derivatives. Martin Schenck (*Arch. Pharm.*, 1909, **247**, 490—506).—Erlenmeyer showed that cyanamide is an intermediate product in the formation of guanidine from cyanogen chloride and alcoholic ammonia. Cyanamide has hitherto not been detected as an intermediate product in the reaction between cyanogen iodide and alcoholic ammonia, but by allowing a mixture of the two to remain at the ordinary temperature for several days, the author has detected cyanamide in the reaction product in the form of its characteristic yellow silver derivative. The formation of guanidine, therefore, probably occurs thus: (1) $NCl + 2NH_3 = NC\cdot NH_2 + NH_4I$; (2) $NC\cdot NH_2 + NH_4I = (NH_2)_2C:NH,HI$. By a similar process, cyanogen iodide and 10% alcoholic methylamine (3 mols.), after being heated for several hours in a closed vessel in steam, yield *s*-dimethylguanidine, of which the platinichloride has m. p. 197°, and the aurichloride, 122°. Under the preceding conditions there is practically no reaction between cyanogen iodide and alcoholic dimethylamine. Ethylenedi-

amine ($\frac{1}{2}$—1 mol.), however, yields ethyleneguanidine (2-iminotetrahydroglyoxaline), $\begin{matrix}CH_2\cdot NH\\ |\\ CH_2\cdot NH\end{matrix}>C{:}NH$, of which the *platinichloride*, $2C_3H_7N_3,H_2PtCl_6$, decomposing at 190°, *picrate*, m. p. 219°, and *aurichloride*, $C_3H_7N_3,HAuCl_4$, m. p. 210°, have been prepared. In a similar way, alcoholic propylenediamine (less than 1 mol.) and cyanogen iodide yield propyleneguanidine (2-imino-4-methyltetrahydroglyoxaline), $\begin{matrix}CHMe\cdot NH\\ |\\ CH_2---NH\end{matrix}>C{:}NH$, the *platinichloride* of which has m. p. 194—195°, and the *aurichloride*, m. p. 100°. Under the some conditions, cyanogen iodide and trimethylenediamine yield a solution from which a crystalline platinichloride, aurichloride, or picrate has not been obtained. Cyanogen iodide and alcoholic aniline, heated in steam for several hours, yield only *p*-iodoaniline (compare Rabe, *Ber.*, 1877, 10, 1717).

A guanidine derivative has not been obtained by the interaction of cyanogen iodide and glycine or its ethyl ester. C. S.

Glycinamide. Martin Schenck (*Arch. Pharm.*, 1909, **247**, 506—515).—Glycinamide is best prepared by keeping a mixture of chloroacetamide and ten times the quantity of 30% ammonium hydroxide in a closed vessel for fourteen days; the excess of ammonia is removed by evaporation, by gently warming in a basin, and finally drying the hydrochloride in a desiccator. A solution of the free base is obtained by means of silver oxide. An alcoholic solution of glycinamide is obtained by keeping ethyl glycine and a large excess of 5% alcoholic ammonia in a closed vessel for two to three weeks, then filtering, and freeing the filtrate from the excess of ammonia by a current of dry purified air. A guanidine derivative could not be obtained by the interaction of the aqueous or alcoholic solution of glycinamide and cyanogen iodide either at the ordinary temperature or by heating (compare preceding abstract), owing to the decomposition of the glycinamide into ammonia and glycine. C. S.

New Synthesis of Aminohydroxy-acids and of Piperidone Derivatives. Emil Fischer and Géza Zemplén (*Ber.*, 1909, **42**, 4878—4892).—The authors show that many ordinary α-bromo-acids, for example, α-bromopropionic, α-bromo*iso*valeric, α-bromo*iso*hexoic, α-bromodihydrocinnamic, are converted to the extent of 70—90% into the hydroxy-acid by boiling their aqueous solutions with calcium carbonate. The reaction has also been applied in the following directions. α-Bromo-δ-*m*-nitrobenzoylaminovaleric acid (Abstr., 1909, i, 303), when boiled with water and calcium carbonate, yields 57% of crystalline *calcium α-hydroxy-δ-m-nitrobenzoylaminovalerate*, $Ca(C_{12}H_{12}O_6N_2)_2,4H_2O$, m. p. 80° in its water of crystallisation. The free acid is a yellow oil, which is hydrolysed by boiling barium hydroxide or 5*N*-hydrochloric acid (and subsequent treatment with silver oxide), yielding *δ-amino-α-hydroxyvaleric acid*,

$$NH_2\cdot[CH_2]_3\cdot CH(OH)\cdot CO_2H,$$

m. p. 188—191° (decomp., corr.), which does not form proline by

treatment with hydrochloric acid or a copper salt with copper oxide. It appears to be a general rule that aqueous solutions of α- and β-, but not those of γ-, δ-, or ε-, amino-acids yield copper salts by boiling with copper oxide. By esterifying δ-amino-α-hydroxyvaleric acid by methyl alcohol and hydrogen chloride, and dechlorinating the ester-hydrochloride by silver oxide, or better by heating the acid at 190°, the lactam, *3-hydroxy-2-piperidone*, $NH<^{CO\cdot CH(OH)}_{CH_2---CH_2}>CH_2$, m. p. 141—142° (corr.), is obtained, which forms a *platinichloride*, m. p. 160° (decomp.). In a similar manner, by esterification with methyl alcohol and hydrogen chloride and subsequent treatment with silver oxide, δ-aminovaleric acid yields 2-piperidone, and *i*-ornithine yields 3-amino-2-piperidone, which forms a *hydrochloride*, $C_5H_{10}ON_2,HCl$, sintering at 220° and melting completely at 250° (decomp.), *platinichloride*,

$$2C_5H_{10}ON_2,H_2PtCl_6,H_2O,$$

decomposing at 200—205°, *picrate*, m. p. 160—162° (corr.), and is reconverted into ornithine by prolonged heating with 20% hydrochloric acid at 100°.

The following compounds are obtained from α-bromo-ε-benzoylaminohexoic acid (Braun, Abstr., 1909, i, 229) by a similar series of reactions: *calcium α-hydroxy-ε-benzoylaminohexoate*, a white, crystalline powder; *α-hydroxy-ε-benzoylaminohexoic acid*, m. p. 108° (corr.); *ε-amino-α-hydroxyhexoic acid*, m. p. 225—230° (decomp., corr.), which does not yield a compound analogous to hydroxypiperidone. C. S.

Catalytic Action of Amino-acids, Peptones, and Proteins in Effecting Certain Syntheses. Henry D. Dakin (*J. Biol. Chem.*, 1909, **7**, 49—56).—Many condensations, possibly analogous to those occurring in living cells, may be brought about by the use of amino-acids, peptones, proteoses, or even proteins as catalysts. For example, furfuraldehyde when warmed with malonic acid does not undergo condensation, but if glycine or alanine is added, considerable amounts of furfuracrylic acid are formed. Attempts, however, to bring about certain other types of condensation (for example, the aldol condensation, condensation between aldehydes and ketones, etc.) by the same means failed. W. D. H.

Molybdenum Cyanides. Arthur Rosenheim, Abraham Garfunkel, and F. Kohn (*Zeitsch. anorg. Chem.*, 1909, **65**, 166—177).—Potassium molybdenum cyanide, $K_4Mo(CN)_8,2H_2O$ (Chilesotti, Abstr., 1905, i, 177), contains the only known stable complex ion with a higher co-ordination number than six, and as there is also some doubt as to the valency of the molybdenum, its investigation has been undertaken.

The titration of reduced molybdenum solutions with permanganate is not interfered with by the presence of cyanides if rapidly performed, and the quinquevalence of the molybdenum in these salts is confirmed. A solution containing oxidised molybdenum (Mo^{VI}), manganous salts, and cyanides, however, undergoes a change under the catalytic influence of light, the manganese being partly oxidised by the molybdenum, and the manganous salt of the complex molybdenum

cyanide being precipitated. An excess of permanganate is therefore gradually decolorised if the solutions are exposed to light. The reaction with ammoniacal silver nitrate also proves the molybdenum in $Mo(CN)_8''''$ to be quinquevalent. This can only be brought into harmony with the facts by doubling the molecule, thus making the complex anion $Mo_2(CN)_{16}''''''$.

A reddish-violet complex salt, $4KCN,MoO_2,10H_2O$, was described by Heide and Hofmann (Abstr., 1896, ii, 605) containing quadrivalent molybdenum. The salts of this series become blue on dehydration. They must contain the complex anion $\left[Mo\begin{matrix}(OH)_4\\(CN)_4\end{matrix}\right]''''$, in accordance with which they are only formed in strongly alkaline solution. Evaporation with water converts them into blue salts, containing the anion $\left[Mo\begin{matrix}O_2\\(CN)_4\end{matrix}\right]''''2H_2O$ or $\left[\begin{matrix}O_2\\Mo(H_2O)_2\\(CN)_4\end{matrix}\right]$. Alkali cyanides convert the blue salts into the yellow series, $R_8Mo_2(CN)_{16}$, oxidation taking place.

The *manganese* salt of the yellow series, $Mn_2Mo(CN)_8,8H_2O$, forms bright yellow, glistening leaflets. The *silverammine*, $[Ag_4(NH_3)_2]Mo(CN)_8$, *nickelammine*, $[Ni(NH_3)_4]_2Mo(CN)_8,8H_2O$, and *pyridinium*, $(C_5NH_6)_4Mo(CN)_8$, salts are also described. *Hydromolybdicyanic acid*, $H_4Mo(CN)_8,6H_2O$, is prepared by adding hydrochloric acid, D 1·19, to a concentrated solution of the potassium salt, extracting the precipitate with absolute alcohol, and precipitating with ether in a freezing mixture. The ether oxonium salt is decomposed with water, and precipitated with hydrochloric acid.

The *sodium* salt of the red series, $Na_4[MoO_2(CN)_4]14H_2O$, contains 2 mols. of constitutional water. C. H. D.

Malonyldihydrazones and their Decomposition Products. Carl Bülow and C. Bozenhardt (*Ber.*, 1909, 42, 4784—4802).—Analogous to the condensation of malonyldihydrazide with ethyl acetoacetate to ethylmalonylbishydrazoneacetoacetate (Bülow, Abstr., 1908, i, 253), the condensation of a number of substituted esters of 1 : 3-ketocarboxylic acids has been studied.

The ethyl esters of methyl-, ethyl-, *iso*propyl-, and benzylacetoacetates readily condense with malonyldihydrazide to form compounds of the type : $CH_2(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CHR{\cdot}CO_2Et)_2$.

In a similar manner, methyl- and ethyl-malonyldihydrazides react with unsubstituted ethyl acetoacetate to form products :

$$CHR'(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO_2Et)_2.$$

On the other hand, it was not found possible to prepare dihydrazones of the type : $CHR'(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CHR{\cdot}CO_2Et)_2$, nor could malonyldihydrazide be coupled with ethyldimethylacetoacetate to form :

$$CH_2(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CR_2{\cdot}CO_2Et)_2.$$

Apparently alkyl derivatives of this class must contain at least four symmetrically distributed hydrogen atoms.

Ethyl malonylbishydrazoneacetoacetate when boiled with water loses a part of the ethyl acetoacetate, and 3-methyl-5-pyrazolone and an insoluble compound, considered to be a polymeride of *cyclo*malonic acid hydrazide, $CH_2<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NH\end{matrix}$, are formed. This is difficult to analyse, but forms hydrazine and malonic acid on hydrolysis, and may be synthesised from malonyldihydrazide by prolonged boiling with acetic acid.

Sodium acetate solution acts similarly to water towards ethyl malonylbishydrazoneacetoacetate. Phenylhydrazine decomposes it into malonyldihydrazide and 1-phenyl-3-methyl-5-pyrazolone, which is converted on boiling with ferric chloride into pyrazole-blue. Potassium hydroxide converts it into malonic acid and 3-methyl-5-pyrazolone. Acetic anhydride forms diacetyldimalonylhydrazide; dilute sulphuric acid decomposes it into malonic acid and hydrazine. Benzaldehyde interacts, forming ethyl acetoacetate and bisbenzylidenemalonyldihydrazine.

Resorcinol and cold concentrated sulphuric acid convert it into malonic acid, hydrazine sulphate, and β-methylumbelliferone.

Ethyl malonylbishydrazoneacetoacetate when kept for four months in water at the ordinary temperature decomposes, forming ethyl 3-methyl-5-pyrazolone-4-*iso*propylenecarboxylate, malonic acid, and polymeric *cyclo*malonyl hydrazide. The carboxylic acid when heated is converted into the δ-lactone of 5-hydroxy-3-methylpyrazole-4-*iso*propylenecarboxylic acid (Abstr., 1908, i, 579), which may also be obtained on slowly heating ethyl malonylbishydrazoacetoacetate in a metallic bath above 125°.

Polymeric cyclo*malonylhydrazide*, $C_3H_4O_2N_2$, is obtained as a grey, amorphous powder, m. p. 266—267°. It is hydrolysed by sodium hydroxide, concentrated sulphuric acid, or sodium acetate to hydrazine and malonic acid.

Ethyl malonylbishydrazonemethylacetoacetate, prepared from malonyldihydrazide and ethyl methylacetoacetate, separates in crystals, m. p. 109—110°.

Ethyl malonylbishydrazone-ethylacetoacetate is a colourless, microcrystalline powder, m. p. 106—106·5°.

Ethyl malonylbishydrazone-isobutylacetoacetate has m. p. 104—105°.

Ethyl malonylbishydrazonebenzylacetoacetate forms colourless needles, m. p. 129—130°.

Ethyl malonylbishydrazoneoxalacetate, prepared from malonyldihydrazide and ethyl oxalacetate, is obtained as a glistening mass of large, matted needles, m. p. 127°.

Ethyl monomethylmalonylbishydrazoneacetoacetate separates in colourless aggregates of snow-like crystals, m. p. 92—93°.

Ethyl monoethylmalonylbishydrazoneacetoacetate, prepared from monoethylmalonyldihydrazide and ethyl acetoacetate, crystallises in small, colourless needles, m. p. 104—104·5°.

Monoethylmalonyldihydrazide is obtained from ethyl monoethylmalonate and hydrazine hydrate in long, matted needles, m. p. 166°.

E. F. A.

Synthesis of Hexahydrocymene [*p*-Methylpropyl*cyclo*hexane]. Wladimir A. Smirnoff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1374—1375).—p-*Tolyldimethylcarbinol*, $C_6H_4Me\cdot CMe_2\cdot OH$, prepared by the action of magnesium methyl iodide on *p*-tolyl methyl ketone, is a colourless liquid with a marked odour, b. p. 109°/15 mm., D_4^{20} 0·9769, n_D^{20} 1·5162. When reduced by means of hydrogen in presence of nickel at 150°, it yields hexahydrocymene [*p*-methylpropyl*cyclo*hexane], $C_{10}H_{20}$, b. p. 170—172°/755 mm., D_4^{20} 0·7974, n_D^{20} 1·4380, which corresponds closely in properties with the menthane obtained by Zelinsky by the reduction of menthene by means of hydrogen in presence of nickel. The investigation is being continued.

T. H. P.

New Space Representation of the Benzene Molecule. John C. Earl (*Chem. News*, 1909, **100**, 305).—The representation in question consists of an octahedron with three sides removed, the remaining sides representing bonds linking the carbon atoms, the linking of the various carbon atoms being the same as in Ladenburg's prism formula. The formula represents satisfactorily the general behaviour of benzene and its derivatives. From it, theoretically only one mono-substitution product, one meta-di- and one para-di-substitution product, but two ortho-disubstitution products, can be formed, and di-, tetra-, and hexa-hydro-derivatives can exist without rupturing the ring.

G. S.

Presence of Ethylene Linkings in Benzene and its Homologues. K. W. Charitschkoff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1152—1154).—The oxidation of mesitylene by means of air in presence of powdered sodium hydroxide (compare Abstr., 1909, i, 154, 471) yields 1·17% of a monobasic acid, $C_9H_{11}\cdot CO_2H$, formed by the oxidation of one of the methyl groups. With *o*-, *m*-, and *p*-xylenes, under similar conditions, only very small proportions of acids are obtained. Hence, the degree of oxidisability of benzenoid hydrocarbons is independent of isomerism in the aromatic nucleus. This result, which is partly confirmed by the investigations on cymene and *ψ*-cymene, supports the conclusion that ethylene linkings are absent from benzene and its homologues, quite independently of the position of the substituent groups. These observations appear to give final confirmation to the diagonal structural formula for benzene and its homologues, which is supported by thermochemical data and by the action of reducing agents, such as hydrogen iodide, the reduction being accompanied by complete transformation of the six-membered ring into one containing five members. The author regards the supposed support given to the Kekulé formula by the action of ozone on benzene and its homologues as ill-founded, the compounds formed as the result of such action being peroxidic in character.

T. H. P.

Derivatives of Phenyldi*cyclo*hexylmethane. Marcel Godchot (*Compt. rend.*, 1909, **149**, 1137—1139).—When phenyldi*cyclo*hexylmethane (Abstr., 1909, i, 19) is dissolved in fuming nitric acid, it undergoes conversion into *nitrophenyldicyclohexylmethane*,

$$NO_2\cdot C_6H_4\cdot CH(C_6H_{11})_2,$$

pale yellow needles, m. p. about 113°.

Phenyldicyclohexylcarbinol, $CPh(C_6H_{11})_2 \cdot OH$, has been obtained by the action of ethyl benzoate on magnesium *cyclo*hexyl bromide; it crystallises in prisms, m. p. 77°, and also with $1\frac{1}{2}$ mols. alcohol in prisms, m. p. 55°. Unlike triphenylcarbinol, it does not combine with aniline, phenol, or hydroxylamine. When distilled in a vacuum, the carbinol loses water, yielding a *hydrocarbon*, $C_6H_{11} \cdot CPh{:}C_6H_{10}$. *Dinitrophenyldicyclohexylmethane*, $NO_2 \cdot C_6H_4 \cdot C(C_6H_{11})_2 \cdot NO_2$, m. p. 150°, arises from the action of fuming nitric acid on the foregoing carbinol, whilst under the same conditions the hydrocarbon yields a *mononitro*-derivative, m. p. 130°. W. O. W.

Carbonium Perchlorates. Karl A. Hofmann and Heinz Kirmreuther (*Ber.*, 1909, **42**, 4856—4865).—Coloured salts and molecular compounds of triphenylcarbinol and its derivatives have recently received much attention in connexion with the problem of colour and constitution, but hitherto salts of triphenylcarbinol and oxy-acids have not been obtained in a crystalline form directly from their components. The authors find that perchloric acid yields beautifully crystalline derivatives with triphenylcarbinol, phenolphthalein, fluorescein, and distyryl ketone. The acid is a 71% solution, obtained by evaporating the commercial acid until the temperature is 136° and then distilling.

Hydrated *triphenylmethyl perchlorate*, $CPh_3 \cdot ClO_4, H_2O$, is obtained by adding 6 c.c. of 71·5% perchloric acid to an ethereal solution of 2 grams of the carbinol. It crystallises in deep yellow octahedra with a blue shimmer, and decomposes by heating or by the addition of water. *Triphenylmethyl perchlorate*, $CPh_3 \cdot ClO_4$, obtained by the addition of 71% perchloric acid to a cold solution of the carbinol in acetic anhydride, crystallises in octahedra, which are brownish-yellow to brownish-red by transmitted light and blue by reflected light. The same substance is apparently produced when a mixture of perchloric acid and ethereal triphenylmethyl chloride is evaporated over sulphuric acid; when the evaporation is performed in an atmosphere of hydrogen chloride, citron-yellow octahedra with a blue lustre are obtained of a mixed salt, $2CPh_3 \cdot Cl, CPh_3 \cdot ClO_4$.

Phenolphthalein perchlorate, $C_{20}H_{14}O_4 \cdot ClO_4, H_2O$, obtained from its components, forms dichroic crystals, which are ruby-red by transmitted and pale blue by reflected light; it is instantly decomposed by water. *Fluorescein diperchlorate*, $C_{20}H_{12}O_5, 2HClO_4$, obtained in a similar manner, is a yellow powder.

[With H. Lecher.]—*Distyryl ketone perchlorate*, $C_{17}H_{14}O, HClO_4$, is precipitated as a red powder by the addition of 71% perchloric acid to ethereal distyryl ketone. After being dried in a vacuum over phosphoric oxide, the substance is orange-red; it is instantly decomposed by water. C. S.

Cryoscopy of Organic Mixtures and Additive Compounds. Abel Buguet (*Compt. rend.*, 1909, **149**, 857—858).—Additive compounds of acenaphthene with α-trinitrotoluene and 2 : 4-dinitrotoluene melt at 109° and 60° respectively, and the compound of phenanthrene with α-trinitrotoluene at 84°. Complete freezing-point curves of

mixtures of these hydrocarbons and nitro-compounds take the form of a W, showing two eutectics and a maximum at the compound.

In the following cases, no compound being formed, the freezing-point curve is a V, showing one eutectic: phenanthrene with 2 : 4-dinitrotoluene and α-nitronaphthalene; acenaphthene with *p*-nitrotoluene; naphthalene with *p*-nitrotoluene, α-nitronaphthalene, acenaphthene, benzoic acid, salicylic acid, azobenzene, diphenylamine, guaiacol, chloral hydrate, menthol, methyl oxalate, phenanthrene, salol, and thymol.

R. J. C.

p-**Hydroxyphenylethylamine.** Karl W. Rosenmund (*Ber.*, 1909, 42, 4778—4783. Compare Barger, Trans., 1909, 95, 1123, 2193).—A relatively simple synthesis of *p*-hydroxyphenylethylamine is effected by condensing anisaldehyde with nitromethane to β-nitro-*p*-methoxystyrene, which can be directly reduced to *p*-methoxyphenylethylamine. It is preferable first to isolate the oxime of *p*-methoxyphenylacetaldehyde and reduce this to the amine. The methoxyl group is eliminated by boiling with decolorised hydriodic acid. The base is obtained by this method in good yield and in a pure state.

β-Nitro-p-methoxystyrene, $OMe\cdot C_6H_4\cdot CH:CH\cdot NO_2$, crystallises in long, yellow needles, m. p. 86—87°. It may be reduced with aluminium amalgam, or with zinc dust and acetic acid, to the oxime of *p*-methoxyphenylacetaldehyde, m. p. 120°, which is conveniently further reduced with sodium amalgam and alcoholic acetic acid. *p-Methoxyphenylethylamine* has a fish-like odour, b. p. 136—138°/18 mm. It forms a *carbonate* on exposure to the atmosphere. The hydrochloride has m. p. 207°.

p-Hydroxyphenylethylamine was obtained in glistening, colourless needles or plates, m. p. 160°; the *hydroiodide* forms yellow needles.

E. F. A.

Molecular Weights of Liquid Diphenylamine, Triphenylamine, and Aniline Hydrochloride. Marie Przyluska (*J. Chim. Phys.*, 1909, 7, 511—533. Compare Renard and Guye, Abstr., 1907, ii, 334).—The surface-tensions of the three substances have been measured by Ramsay and Shield's method at a number of temperatures between their melting and boiling points. Diphenylamine distilled at atmospheric pressure gave irregular results, but after fractional distillation at 50 mm. pressure, the surface-tensions indicated a unimolecular constitution. The somewhat different conclusion arrived at by Dutoit and Friderich (Abstr., 1900, ii, 194) may have been due to products of decomposition in their material.

Diphenylamine gives normal b. p. elevations in benzene or acetone, whereas Kahlenberg found it to be dissociated in acetonitrile. The surface-tension of diphenylamine indicates that its critical temperature would be 560° if it were not decomposed by heat.

Triphenylamine is polymerised to an increasing degree as the temperature rises from 108° to 335°, in agreement with the known tendency of such hydrocarbons to give condensation products on heating. Aniline hydrochloride passes directly at its boiling point (243°) from a polymerised liquid to a dissociated gaseous form.

R. J. C.

Action of Thiocarbimides on Alcohols and Mercaptans. I. New Method for Obtaining Mono-substituted Thio- and Dithiocarbamates of Monatomic Alcohols and Mercaptans. M. S. Roschdestvensky (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1438—1454. Compare Abstr., 1909, i, 300).—Methyl phenylthiocarbamate, prepared by the action of sodium methoxide on phenylthiocarbimide, has m. p. 92·5—93·5° (Orndorff and Richmond, Abstr., 1900, i, 156, gave 97°). The corresponding ethyl derivative has m. p. 68—69° (Orndorff and Richmond, *loc. cit.*, gave 71—72°).

Allyl phenylthiocarbamate, $NHPh\cdot CS\cdot O\cdot C_3H_5$, forms aggregates of long needles, m. p. 64·5—65·5°; the *menthyl* ester,

$$NHPh\cdot CS\cdot O\cdot C_{10}H_{19},$$

has m. p. 74—75°, $[\alpha]_D^{20}$ −63·07°; the *benzyl* ester,

$$NHPh\cdot CS\cdot O\cdot CH_2Ph,$$

has m. p. 82—82·5°.

Methyl β-naphthylthiocarbamate, $C_{10}H_7\cdot NH\cdot CS\cdot OMe$, prepared by the action of sodium methoxide on β-naphthylthiocarbimide, forms pale, cinnamon-coloured crystals, m. p. 104—105°. The *propyl* ester has m. p. 83—84°.

Methyl allylthiocarbamate, $C_3H_5\cdot NH\cdot CS\cdot OMe$, obtained by the action of sodium methoxide on allylthiocarbimide, is a brownish-yellow, mobile liquid with a peculiar odour, b. p. 121—122°/27 mm., D_{20}^{20} 1·0811, D_4^{20} 1·0792, n_D^{20} 1·5379; it combines readily with bromine, giving a crystalline product.

Bornyl allylthiocarbamate, $C_3H_5\cdot NH\cdot CS\cdot O\cdot C_{10}H_{17}$, forms white crystals, m. p. 59—60°, $[\alpha]_D^{20}$ +14·25°.

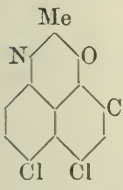
Methyl phenyldithiocarbamate, $NHPh\cdot CS\cdot SMe$, prepared by the interaction of methyl mercaptan and phenylthiocarbimide in presence of sodium hydroxide, has m. p. 95—96° (compare Will, Abstr., 1882, 723; Losanitsch, Abstr., 1892, 55). The *ethyl* ester has m. p. 60—61° (Hofmann, *Ber.*, 1869, 2, 120, gave 56°, and Will, Abstr., 1882, 1088, gave 60°). The *propyl* ester,

$$NHPh\cdot CS\cdot SPr^{\alpha},$$

which may be prepared either in aqueous solution or in absence of water, has m. p. 66—67°.

Methyl β-naphthyldithiocarbamate, $C_{10}H_7\cdot NH\cdot CS\cdot SMe$, has m. p. 116—117°. T. H. P.

8-Amino-1-naphthol. II. Fritz Fichter and Theodor Kühnel (*Ber.*, 1909, 42, 4748—4752. Compare Abstr., 1906, i, 839).—Chlorine reacts with an acetone solution of 8-acetylamino-1-naphthol in much the same manner as bromine (*loc. cit.*, 840), yielding a crystalline precipitate of 6 : 7 : 9-*trichloro-2-methylperinaphthoxazole* (annexed formula) in the form of greenish-coloured needles, which do not melt below 300°.



8-*Acetylamino*-1-*naphthoxyacetic acid*,

$$NHAc\cdot C_{10}H_6\cdot O\cdot CH_2\cdot CO_2H,$$

obtained by condensing 8-acetylamino-1-naphthol with a concentrated aqueous solution of chloroacetic acid and potassium hydroxide, forms long, colourless needles, m. p. 245°. The *cupric* salt, $(C_{14}H_{12}O_4N)_2Cu$,

forms slender, pale blue needles. When boiled with alkalis or acids, the acid does not yield a ring compound as the isomeric 1-acetylamino-2-naphthoxyacetic acid does (Spitzer, Abstr., 1901, i, 715).

The nitro-derivative obtained by the action of nitric acid on 8-acetylamino-1-naphthyl acetate is now shown to be the 5-nitro-derivative. This has been proved by hydrolysing the product to nitro-8-acetylamino-1-naphthol, the methyl ether of which when hydrolysed, diazotised, and boiled with alcohol gives the same methyl ether as is obtained by the action of methyl sulphate on 5-nitro-1-naphthol (Kaufler and Bräuer, Abstr., 1907, i, 799). 5-Nitro-8-acetylamino-1-naphthol changes colour at 192°, but has m. p. 240°

4-*Benzeneazo*-5-*nitro*-8-*acetylamino*-1-*naphthol*, $C_{18}H_{14}O_4N_4$, obtained by condensing benzenediazonium chloride with an alcoholic alkaline solution of the 5-nitro-8-acetylamino-1-naphthol, forms dark red crystals with a metallic lustre and m. p. 220°.

5-*Nitro*-8-*amino*-1-*naphthyl methyl ether*, $C_{11}H_{10}O_3N_2$, forms large, reddish-brown crystals, m. p. 193°. 5-*Nitro*-1-*naphthyl methyl ether*, $C_{11}H_9O_3N$, forms slender, yellow needles, m. p. 96—97°.

When α-naphthyl acetate is nitrated at 0° with nitric acid (D 1·38), a 60% yield of 2:4-dinitro-1-naphthol and a 5% yield of 2-nitro-1-naphthyl acetate are obtained.

8-*Tolylsulphonylamino*-1-*naphthol*, $OH\cdot C_{10}H_6\cdot NH\cdot SO_2\cdot C_7H_7$, obtained by heating 8-amino-1-naphthol sulphate, *p*-toluenesulphonyl chloride, and sodium acetate with acetic acid, forms colourless prisms, m. p. 189°.

8-*Acetylamino*-1-*naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot NHAc$, crystallises in broad, glistening plates, m. p. 154. J. J. S.

Compounds of Hexamethylenetetramine with Multivalent Alcohols. E. Grishkewitsch-Trochimowsky (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1324—1325).—Hexamethylenetetramine reacts with multivalent alcohols, forming crystalline, complex compounds, which are deposited in almost quantitative yield when aqueous solutions of the amine and alcohol are mixed.

Resorcinol gives the *compound*, $C_6H_{12}N_4,C_6H_4(OH)_2$, which forms shining, oblique prisms, begins to turn yellow at 125°, and decomposes completely at about 200°.

Catechol yields the *compound*, $C_6H_{12}N_4,2C_6H_4(OH)_2$, in slender needles, decomp. about 160°.

Pyrogallol gives the *compound*, $2C_6H_{12}N_4,3C_6H_3(OH)_3$, forming small needles, decomp. about 145°. T. H. P.

Tertiary Alcohols of the Tolylallyl Series. E. Grishkewitsch-Trochimowsky (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1326—1332. Compare Abstr., 1909, i, 151).—p-*Tolylethylallylcarbinol*,

$$C_6H_4Me\cdot CEt(CH_2\cdot CH{:}CH_2)\cdot OH,$$

prepared by the action of magnesium on a mixture of *p*-tolyl ethyl ketone and allyl bromide, is a yellow, viscous liquid with an intense, characteristic odour, b. p. 133—135°/18 mm., D_4^{22} 0·9664, n_D^{22} 1·52093. On oxidation, it gives the corresponding acid and trihydric alcohol, to be described later.

The intermediate *organo-magnesium compound*,

$$C_6H_4Me\cdot CEt(C_3H_5)\cdot O\cdot MgBr,OEt_2,$$

formed in the above reaction, separates in almost colourless prisms.

p-*Tolylpropylallylcarbinol*, $C_6H_4Me\cdot CPr^{\alpha}(C_3H_5)\cdot OH$, prepared by the action of magnesium on a mixture of *p*-tolyl propyl ketone and allyl bromide, is a viscous, colourless liquid with an intense, characteristic odour, b. p. 138—139°/13 mm., D_4^{20} 0·9531, n_D^{20} 1·51682.

p-*Tolyl*isopropylallylcarbinol, $C_6H_4Me\cdot CPr^{\beta}(C_3H_5)\cdot OH$, obtained by the action of magnesium on a mixture of *p*-tolyl *iso*propyl ketone and allyl bromide, is a viscous, colourless liquid of aromatic odour, b. p. 140—143°/21 mm., $D_4^{19\cdot5}$ 0·9542, $n_D^{19\cdot5}$ 1·51385.

Comparison of the physical constants of these alcohols and those of *p*-tolylmethylallylcarbinol (*loc. cit.*) shows that passage from any one member of the series to the next higher homologue is accompanied by a rise of 5—7° in the b. p., a diminution of 0·017—0·013 in the value of D, an increase in the value of n, and an increase of about 5 in the molecular refraction (Lorenz and Lorentz's formula). Isomeric alcohols of this series differ but slightly in b. p., and have almost identical values for D and for the molecular refraction.

T. H. P.

Action of Magnesium on a Mixture of Allyl Bromide and Benzophenone: Synthesis of Diphenylallylcarbinol. B. Tarasoff (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1309—1313).—Diphenylallylcarbinol, $C_3H_5\cdot CPh_2\cdot OH$ (compare Javorsky, Abstr., 1908, i, 753), is a viscous, pale yellow liquid with a characteristic odour and a bitter taste, b. p. 300°/760 mm. (decomp.), 183—184°/27 mm., $D_4^{23\cdot8}$ 1·0720, $n_D^{23\cdot8}$ 1·59179. It decolorises bromine readily, and on oxidation with 1·5 times the theoretical proportion of potassium permanganate, yields *αα-diphenylbutane-αγδ-triol*,

$$OH\cdot CPh_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

which crystallises in small, pale yellow, hygroscopic needles, m. p. 136—137°.

More vigorous oxidation of diphenylallylcarbinol (1 mol.) by means of permanganate (4 atoms of oxygen) yields *β*-hydroxy-*ββ*-diphenylpropionic acid (compare Rupe and Busolt, Abstr., 1908, i, 23).

In one instance the action of magnesium on a mixture of allyl bromide and benzophenone yielded, instead of diphenylallylcarbinol, a product which, when distilled under diminished pressure, gave water and then a heavy, dark red liquid, b. p. about 290—292°, with a characteristic hydrocarbon odour. T. H. P.

Action of Magnesium on a Mixture of Phenyl *p*-Tolyl Ketone and Allyl Bromide. W. Kuzmin (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1314—1319).—*Phenyl*-p-*tolylallylcarbinol*,

$$C_6H_4Me\cdot CPh(OH)\cdot CH_2\cdot CH{:}CH_2,$$

obtained by the action of magnesium on a mixture of allyl bromide and phenyl *p*-tolyl ketone, is a colourless liquid, b. p. 201—202°/30 mm.

α-Phenyl-α-p-tolylbutane-αγδ-triol,

$$C_6H_4Me\cdot CPh(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

prepared by oxidising phenyl-*p*-tolylallylcarbinol with 1% permanganate solution, forms nodular crystals, m. p. 149—150°.

β-Hydroxy-β-phenyl-β-p-tolylpropionic acid,

$$C_6H_4Me\cdot CPh(OH)\cdot CH_2\cdot CO_2H,$$

prepared by oxidising phenyl-*p*-tolylallylcarbinol by means of 4% permanganate solution, forms rosettes or nodular masses of acicular crystals, and begins to decompose at 181°. Its *silver*, *potassium*, and *copper* salts were prepared. T. H. P.

Structure of Naphthenic Acids. K. W. Charitschkoff (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1150—1152).—The structure of the naphthenic acids isolated from natural naphtha still remains undecided, descriptions which have been given of these acids often containing no information concerning either their characteristic reactions or their derivatives. These acids exhibit distinctly acid properties, forming stable salts with many metallic oxides, and, in some cases, displacing mineral acids, for example, from copper and silver salts; whilst, on the other hand, they present the properties of anhydrides and alcohols, as they give Rosenthaler's reaction with hydrochloric acid and vanillin, and form chloro-anhydrides, which are decomposed with difficulty by water, or an alkali yielding the corresponding acids, together with compounds of unknown constitution resembling simple ethers. The formula,

$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!CH\cdot[CH_2]_4\cdot CH\!<\!\begin{matrix}CH_2\\ |\\ O\end{matrix}\!\!>\!CH\cdot OH,$$

given by Zalozetzky, and the one,

$$\begin{matrix}CH_2\cdot CHMe\\ |\\ CH_2\text{---}CH_2\end{matrix}\!\!>\!CH\cdot CH\!<\!\begin{matrix}CH_2\cdot CH_2\\ |\ \ \ |\\ O\text{---}CH\cdot OH\end{matrix},$$

given by Brun (Wischin, *Die Naphtene*, 28), and also other formulæ which have been given for decanapthenic acid, do not explain the acidic function possessed by the hydroxyl group.

The suggestion is made that *cyclo*hexane-3-acetic acid,

$$C_6H_{11}\cdot CH_2\cdot CO_2H$$

(compare Zelinsky and Alexandroff, Abstr., 1902, i, 74), may be capable of existing in a tautomeric modification having the formula

$$C_6H_{11}\cdot CO\cdot CH_2\cdot OH,$$

which would explain the alcoholic properties exhibited by the acid. T. H. P.

Synthesis of Aromatic Amino-acids. IV. Direct Carboxylation of Dimethylaniline in the Nucleus. Rearrangement of Alkylphenylcarbonates into *p*- and *o*-Alkylaminobenzoates. Josef Houben and Robert Freund (*Ber.*, 1909, 42, 4815—4825).—The formation of dimethylaminobenzoic acid when methylaniline, alkyl iodide, magnesium and carbon dioxide are heated at 200° in presence of dimethylaniline suggests that the last substance acts as a methylating agent, and that possibly the introduction of the group CO_2MgI into the nucleus of methylaniline facilitates the

methylation of the methylamino-group. On the other hand, no methylaminobenzoate is formed on prolonged heating of magnesium aminobenzoate with dimethylaniline. Probably magnesium methyl iodide and dimethylaniline first interact, forming methane and iodomagnesiumdimethylaniline, $IMg{\cdot}C_6H_4{\cdot}NMe_2$, and this forms an additive compound with carbon dioxide, yielding the *p*-dimethylaminobenzoate. In agreement with this hypothesis, the salt of *p*-dimethylaminobenzoic acid is formed when *p*-toluidine, dimethylaniline, and methyl magnesium iodide are heated in a stream of carbon dioxide at 190—200°. *p*-Dimethylaminobenzoic acid is formed when magnesium methyl iodide and dimethylaniline are heated in carbon dioxide at 215° in open vessels or under pressure. The formation of an inflammable gas, probably methane, was also observed.

No salt of *p*-dimethylaminobenzoic acid is formed when dimethylaniline is heated with iodomagnesium acetate or formate, with or without carbon dioxide; this disposes of the possibility that carbon dioxide and magnesium methyl iodide first react to form iodomagnesium acetate.

p-Dimethylaminobenzoic acid is the main product when carbon dioxide and methylaniline magnesium iodide are heated under considerable pressure, but at the same time small quantities of an *o*-methylamino-acid are formed, crystallising in well formed blue, glistening needles, and fluorescing blue in alcoholic solution; this is probably methylanthranilic acid.

On heating carbon dioxide and ethylaniline magnesium iodide, a mixture of *p*-diethylaminobenzoic acid, m. p. 193°, and *p*-ethylaminobenzoic acid, together with traces of methylanthranilic acid, is obtained.

When carbon dioxide is heated at 220° under 10 atmospheres pressure with magnesium ethyl iodide and a mixture of mono- and di-ethylaniline, both *p*-diethylaminobenzoic acid, m. p. 190°, and p-*ethylaminobenzoic acid*, m. p. 177—178°, are formed. p-*Acetylethylaminobenzoic acid* forms colourless platelets, m. p. 180°; the *chloroacetyl* derivative also crystallises in colourless, flat plates, m. p. 163—164°; the *carbethoxy*-compound separates in needles, m. p. 130°. E. F. A.

Benzylamineacrylic Acids (ω-Aminomethylcinnamic Acids). Alfred Einhorn and Maximilian Göttler (*Ber.*, 1909, 42, 4837—4850).—Methylolchloroacetamide and cinnamic acid interact in presence of concentrated sulphuric acid, forming a mixture of ω-chloroacetylamino-*p*- and -*m*-methylcinnamic acids. The two isomerides may be separated by means of acetone, in which the para-derivative is sparingly soluble.

Ethyl ω-chloroacetylamino-*p*-methylcinnamate interacts with diethylamine or piperidine, forming ethyl ω-diethyl- or piperidyl-glycylamino-*p*-methylcinnamate, which is hydrolysed by hydrobromic acid to the corresponding acid.

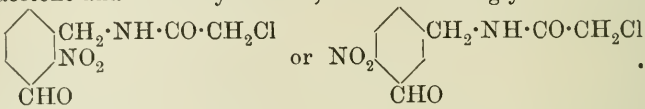
When boiled with hydrochloric acid, ω-chloroacetylamino-*p*-methylcinnamic acid is converted into the hydrochloride of ω-amino-*p*-methylcinnamic acid, from which the free acid is obtained on evaporation

with ammonia. ω-Amino-*p*-methylcinnamic acid forms terephthalic acid on oxidation with permanganate; nitrous acid converts it into *p*-methylolcinnamic acid.

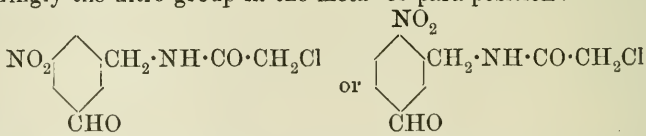
On nitration of ω-chloroacetylamino-*p*-methylcinnamic acid, a mixture of two isomeric mononitro-acids, m. p. 171—172° and 224—225°, is formed.

The less fusible acid is converted into a nitro-ω-chloroacetylamino-*p*-tolualdehyde on oxidation, which, since it is coloured blue by acetone and alkali hydroxide, contains the nitro- and COH-groups in the adjacent positions; therefore it must be *o*-nitro-ω-chloroacetylamino-*p*-methylcinnamic acid; the more fusible isomeride is *m*-nitro-ω-chloroacetylamino-*p*-methylcinnamic acid.

Two mononitro-derivatives are similarly formed from ω-chloroacetylamino-*m*-methylcinnamic acid, m. p. 220° and 198° respectively. The latter gives on oxidation nitro-ω-chloroacetylamino-*m*-tolualdehyde, which forms a claret-red phenylhydrazone and gives a blue coloration with acetone and alkali hydroxide; it has accordingly the formula:



The nitro-acid, m. p. 220°, is the main product; it forms a nitro-aldehyde giving a greenish-red colour with acetone and alkali, and has accordingly the nitro-group in the meta- or para-position:



Cinnamic acid is dissolved in much concentrated sulphuric acid, and methylolchloroacetamide slowly added in the cold; about 70% of the theoretical quantity of the condensation product is obtained. Permanganate oxidises it into a mixture of terephthalic and *iso*phthalic acids, identified by their dimethyl esters. By treatment with acetone the product is separated into *ω-chloroacetylamino*-p-*methylcinnamic acid*, $CO_2H{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, crystallising in well formed needles, m. p. 210°, and *ω-chloroacetylamino*-m-*methylcinnamic acid*, which separates in starch-like, crystalline aggregates, m. p. 152—155°.

The *ethyl* ester of the former crystallises in bunches of intergrown needles, m. p. 106—107°; the *methyl* ester has m. p. 96—97°.

Ethyl ω-diethylglycylamino-p-*methylcinnamate*,

$$CO_2Et{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NEt_2,$$

was obtained as an oil on condensation of the above ester with diethylamine; the *salts* were also oily, with the exception of the *picrate*, which crystallises in golden-yellow plates, m. p. 152°. The *hydrobromide* of the corresponding acid crystallises in fatty, glistening plates, m. p. 211—212°.

Ethyl ω-piperidylglycylamino-p-*methylcinnamate* is a thick fluid oil; the *picrate* crystallises from alcohol in platelets, m. p. 170°. The *hydrobromide* of the acid crystallises in glistening plates, m. p. 226—227°.

ω-Amino-p-*methylcinnamic acid*, $NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$,

crystallises in plates, which do not melt at 320°. The *hydrochloride* forms stellar aggregates of lustrous needles, m. p. 295—296°. The acid interacts with monochloroacetic anhydride, forming the ω-chloroacetyl described above.

ω-Amino-m-*methylcinnamic acid* crystallises in prismatic needles, which darken at 200°, m. p. 243—244° (decomp.). The *hydrochloride* forms quadratic plates or rhomboids.

p-*Methylolcinnamic acid*, $OH\cdot CH_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, prepared by the action of sodium nitrite on the amino-*p*-methylcinnamic acid separates in indefinite, flocculent aggregates or needles, m. p. 200—201°.

2-*Nitro-ω-chloroacetylamino*-p-*methylcinnamic acid* crystallises in colourless needles, m. p. 224—225°; the *ethyl* ester forms very minute needles, m. p. 143—144°.

3-*Nitro-ω-chloroacetylamino*-p-*tolualdehyde* crystallises in minute rhombohedra, m. p. 171° (decomp.). When warmed with concentrated hydrochloric acid, it becomes at first violet-red, later a dirty green, and subsequently a black powder separates. The *phenylhydrazone* forms garnet-red prisms, m. p. 191—192° (decomp.). The aldehyde condenses with acetone in presence of sodium hydroxide to *diketopiperazinobis* (o-*nitro*-p-*methylstyryl methyl ketone*),

$$C_4N_2H_4O_2[CH_2\cdot C_6H_3(NO_2)\cdot CH{:}CH\cdot COMe]_2,$$

crystallising in matted needles, which darken at 230°, m. p. 242° (decomp.).

3-*Nitro-ω-chloroacetylamino*-p-*methylcinnamic acid* forms strongly refractive plates, m. p. 171—172°; the *ethyl* ester forms rectangular platelets, m. p. 105°.

4- or 5'-*Nitro-ω-chloroacetylamino*-m-*methylcinnamic acid* crystallises in needles, m. p. 220°; the *ethyl* ester separates in prisms, m. p. 148—150°.

5- or 6-*Nitro-ω-chloroacetylamino*-m-*tolualdehyde* forms refractive parallelogram-like plates, m. p. 198—199°, and gives an intense red coloration with acetone and alkali. o-*Nitro-ω-chloroacetylamino*-m-*methylcinnamic acid* crystallises in leaflets, m. p. 198°; the *ethyl* ester forms refractive platelets, m. p. 241—242° (decomp.). o-*Nitro-ω-chloroacetylamino*-m-*tolualdehyde* forms bunches of needles, m. p. 125°; it gives an intense blue coloration on warming with acetone and sodium hydroxide. The *phenylhydrazone* crystallises in needles aggregated in bunches, m. p. 174°. E. F. A.

Some Condensation Products from Arylsulphonated Acetonitriles and Aromatic Aldehydes. Julius Tröger and H. Bremer (*Arch. Pharm.*, 1909, 247, 613—617).—The following compounds have been obtained by the method described previously (Abstr., 1908, i, 798); the notation is the same, namely,

$$R\cdot CH{:}C(SO_2R')\cdot CN.$$

$R = p\text{-}C_6H_4\cdot NMe_2$, $R' = Ph$, red needles with blue fluorescence, 194°; $R = p\text{-}C_6H_4Pr^{\beta}$, $R' = Ph$, pale yellow needles, 78°; $R = p\text{-}C_6H_4\cdot OH$, $R' = Ph$, yellowish-white crystals, 214°; $R = p\text{-}C_6H_4\cdot NMe_2$, $R' = \beta\text{-}C_{10}H_7$, red crystals, 197°; $R = p\text{-}C_6H_4Pr^{\beta}$, $R' = \beta\text{-}C_{10}H_7$, large prisms,

146°; R = *p*-C_6H_4·OH, R′ = *β*-$C_{10}H_7$, yellow crystals, 157°; R = *p*-C_6H_4·NH_2, R′ = *p*-C_6H_4Cl, red rhombohedra, 245—246°;
R = *p*-C_6H_4·OH, R′ = *p*-C_6H_4Cl,
yellow prisms, 154—156°; R = *p*-C_6H_4·NMe_2, R′ = *p*-C_7H_7, red crystals with blue fluorescence, 217°; R = *p*-C_6H_4·OH, R′ = *p*-C_7H_7, leaflets, 133—135°; R = *p*-$C_6H_4NMe_2$, R′ = *p*-C_6H_4Br, red prisms with blue shimmer, 240—241°; R = *p*-C_6H_4·OH, R′ = *p*-C_6H_4Br, yellow prisms, 166°; R = *p*-C_6H_4·NMe_2, R′ = *p*-C_6H_4I, ruby-red crystals with blue shimmer, 222°; R = *p*-C_6H_4·NMe_2, R′ = $C_6H_2Me_3$, light red prisms, 192°; R = *p*-C_6H_4·OH, R′ = $C_6H_2Me_3$, yellow prisms, 181°.

C. S.

Halogen-amino-acids. VIII. Position of the Iodine Atoms in Di-iodotyrosine (Iodogorgonic Acid). Henry L. Wheeler and Carl O. Johns (*Amer. Chem. J.*, 1910, **43**, 11—19).—Wheeler and Jamieson (Abstr., 1905, i, 350) synthesised iodogorgonic acid, and showed it to be a di-iodotyrosine, probably the 3 : 5-compound. This configuration has now been confirmed.

Di-iodotyrosine, when treated with methyl iodide and potassium hydroxide, is converted into a *compound*, provisionally regarded as OMe·$C_6H_2I_2$·CH_2·CH(NMe_3I)·CO_2H. On boiling this substance with sodium hydroxide, *sodium* 3 : 5-*di-iodo*-p-*methoxycinnamate* is obtained, and, when acidified with hydrochloric acid, is converted into the corresponding *acid*, OMe·$C_6H_2I_2$·CH:CH·CO_2H, m. p. 202—203°, which forms minute prisms or long, silky needles. This acid has also been prepared by the methylation of 3 : 5-di-iodo-*p*-hydroxycinnamic acid (Paal and Mohr, Abstr., 1897, i, 53), which has m. p. 247° (decomp.). The *potassium*, *barium*, *silver*, *mercury*, and *copper* salts of 3 : 5-di-iodo-*p*-methoxycinnamic acid are described. The *methyl* ester, m. p. 173—174°, crystallises in thin plates, and the *ethyl* ester, m. p. 135°, in small, colourless prisms. E. G.

Conversion of Stable Stereoisomeric Ethylene Derivatives into the Labile Modifications by Ultraviolet Light. Richard Stoermer (*Ber.*, 1909, **42**, 4865—4871).—In connexion with the stereoisomerides of substituted ethylenes, the conversion of the labile into the stable modification by the action of light, particularly in the presence of a halogen, is not uncommon. The converse change, produced by light alone, has been remarked in very few cases (Paal and Schultze, Abstr., 1902, i, 228; Ciamician and Silber, *ibid.*, 1904, i, 161).

Perkin has noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight (Trans., 1881, **39**, 409), but the author finds that in the coumaric acid series the tendency is the other way, the stable form changing to the labile under the influence of ultraviolet light. Thus Perkin's change occurs only to the extent of 25%, whereas coumaric acid yields 75% of coumarin, methylcoumaric acid yields 75% of methylcoumarinic acid, ethylcoumaric acid yields ethylcoumarinic acid quantitatively, and acetylcoumaric acid is also quantitatively changed to acetylcoumarinic acid.

That the changes are caused by the ultraviolet rays is proved by

means of light filters, the interposition of a filter which absorbs ultraviolet light between the lamp and the solution preventing any change of the stable to the labile modification. Hence the less fusible stable forms of stereoisomeric compounds can be changed directly, under definite conditions, into the more reactive labile modifications if energy is supplied by ultraviolet light. Thus the stable form of *o*-anisylcinnamic acid, which could not be changed into the labile modification by Stoermer and Frederici (Abstr., 1908, i, 179), has now been converted to the extent of 50% by using a more intense light. In the case of stereoisomeric *α*-alkylated acids, the conversion of the stable into the labile form is a matter of great difficulty. The case of cinnamic acid is interesting. A benzene solution of ordinary cinnamic acid is exposed for eight days to the light of a Uviol lamp, with the result that 25—30% of Liebermann's *iso*cinnamic acid, m. p. 58°, is produced. *allo*Cinnamic acid in benzene is converted into ordinary cinnamic acid under similar conditions. Also fumaric acid changes to maleic acid in eight days, but the conversion of mesaconic acid into citraconic acid is very difficult, these being *α*-methylated acids. When stilbene in benzene is exposed to ultraviolet light for eight days, it is converted to the extent of about 90% into *iso*stilbene, which can be reconverted into stilbene by heating at 170—180° for one hour, by the vapour of fuming nitric acid in a few minutes, and quantitatively by exposure to sunlight of its solution in carbon disulphide containing a trace of bromine.

C. S.

General Synthesis of Phenylated Fatty Acids. Ferdinand Mauthner (*Annalen*, 1909, 370, 368—375. Compare Abstr., 1908, i, 986).—Derivatives of acetic acid, containing as a substituent either a phenyl or substituted phenyl group, may be prepared from the corresponding aromatic aldehydes by the following series of changes: (1) $R\cdot CHO + NHBz\cdot CH_2\cdot CO_2H = 2H_2O + NBz<\begin{matrix}CO\\|\\C:CHR\end{matrix}$; (2) $NBz<\begin{matrix}CO\\|\\C:CHR\end{matrix} \xrightarrow[NaOH]{Aqueous} NH_3 + Ph\cdot CO_2H + CH_2R\cdot CO\cdot CO_2H$, and (3) $CH_2R\cdot CO\cdot CO_2H + H_2O_2 = H_2O + CO_2 + CH_2R\cdot CO_2H$. The isolation of the substituted pyruvic acid is unnecessary; the solution obtained by boiling the azlactone with a dilute aqueous solution of sodium hydroxide is treated with hydrogen peroxide at the ordinary temperature. In order to exemplify its general applicability, phenylacetic acid, *p*-hydroxyphenylacetic acid, *o*-methoxyphenylacetic acid, *p*-methoxyphenylacetic acid, homovanillic [4-hydroxy-3-methoxyphenylacetic] acid, and homopiperonic [methylenedioxyphenylacetic] acid have been prepared by this method.

The following azlactones are prepared by heating the necessary aldehyde with hippuric acid, acetic anhydride, and sodium acetate on a water-bath. *3-Acetoxy-4-methoxy-(α)-benzoyliminocinnamic anhydride*, $C_{19}H_{15}O_5N$, has m. p. 194—195°. *2-Methoxy-(α)-benzoyliminocinnamic anhydride*, $C_{17}H_{13}O_3N$, crystallises in yellow leaflets, m. p. 165—166°.

W. H. G.

Lactonoid Anhydrides of Acylated Amines. I. The Lactones of Acetylanthranoylanthranilic Acid and of Acetylanthranilic Acid. Ernst Mohr and Friedrich Köhler (*J. pr. Chem.*, 1909, [ii], 80, 521—546).—Anthranoylanthranilic acid, when boiled with excess of acetic anhydride, yields the lactone, $NHAc\cdot C_6H_4\cdot C\overset{N\cdot C_6H_4}{\underset{O\cdot CO}{<}}$, and not acetylanthranoylanthranilic acid (Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57). The formation of this characteristic lactone is one of the best criteria for the recognition of anthranoylanthranilic acid.

Anthranilic acid or acetylanthranilic acid, when heated with acetic anhydride, yields acetylanthranil, $\overset{CMe:N}{\underset{O-CO}{}}>C_6H_4$ (Bredt and Hof, Abstr., 1900, i, 229; Anschütz and Schmidt, *ibid.*, 1903, i, 56), and benzoylanthranilic acid yields a similar lactone (Angeli and Angelico, Abstr., 1901, i, 46; Heller and Fiesselmann, *ibid.*, 1902, i, 780). Thionyl chloride transforms anthranoylanthranilic acid into a lactone, m. p. 162° (Schroeter, Abstr., 1907, i, 530), which reacts with acetic anhydride, yielding acetylanthranoylanthranilic acid lactone.

Benzoylated α-amino-fatty acids are also capable of losing water in a similar manner, yielding lactones (Erlenmeyer, Abstr., 1893, i, 580; 1899, i, 759; 1900, i, 549; compare also Mohr and Geis, Abstr., 1908, i, 339, and Mohr and Stroschein, *ibid.*, 1909, i, 581).

These lactones are intermediate in properties between acid anhydrides and lactones, and belong to Hans Meyer's second class of lactones (Abstr., 1900, i, 9). They combine readily with ammonia, yielding amides of the type $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2$, which lose the elements of water when boiled with sodium hydroxide solution, yielding cyclic imides, for example, $NHAc\cdot C_6H_4\cdot C\overset{N—C_6H_4}{\underset{NH\cdot CO}{<}}$.

The possibility of a lactam structure, $NHAc\cdot C_6H_4\cdot CO\cdot N\overset{C_6H_4}{\underset{CO}{<}}$, for the lactone of acetylanthranoylanthranilic acid is discussed, but rejected (compare Bamberger, Abstr., 1903, i, 432; 1909, i, 509).

Acetylanthranoylanthranilic acid crystallises in colourless needles, m. p. 221·5—222° (Anschütz, Schmidt, and Greiffenberg, 225—226°). The *sodium* salt crystallises in thin, flexible needles. The *lactone*, $NHAc\cdot C_6H_4\cdot C\overset{N\cdot C_6H_4}{\underset{O\cdot CO}{<}}$, crystallises in pale yellow plates or needles, m. p. 211—212°. When warmed with sodium hydroxide solution, it yields ultimately acetic and anthranilic acids. When boiled with alcoholic ammonia, the lactone yields *acetylanthranoylanthranilamide*, $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2$, which crystallises in glistening, snow-white prisms, m. p. 226—227° (decomp.). The *imide*, 2-*o*-*aminophenyl*-3 : 4-*dihydro*-1 : 3-*quinazolone*, $NH_2\cdot C_6H_4\cdot C\overset{N—C_6H_4}{\underset{NH\cdot CO}{<}}$, obtained by boiling the above amide with 6*N*-sodium hydroxide solution and precipitating with acetic acid, crystallises in lemon-

yellow needles, m. p. 237°, and has both feebly basic and acidic properties. The *sodium* salt and the *hydrochloride* have been prepared.

The *acetyl* derivative, $C_{16}H_{13}O_2N_3$, crystallises in very pale yellow prisms, m. p. 278° (decomp.), and yields a sparingly soluble *sodium* derivative.

The name lactimones (Abstr., 1908, i, 339 ; 1909, i, 581) for this type of lactone is withdrawn. J. J. S.

Lactonoid Anhydrides of Acylated Amino-acids. II. Lactone of α-Benzoylamino*iso*butyric Acid. Ernst Mohr [with Theodor Geis] (*J. pr. Chem.*, 1910, [ii], 81, 49—73. Compare Abstr., 1908, i, 339).—A more detailed account of work already published. The lactimone, $CMe_2<\begin{matrix}N=CPh\\ CO\cdot O\end{matrix}$ (*loc. cit.*), is a very reactive substance, yielding *α-benzoylamino*isobutyranilide, $NHBz\cdot CMe_2\cdot CO\cdot NHPh$, m. p. 228—229°, with aniline ; the *chloride*, $NHBz\cdot CMe_2\cdot COCl$, m. p. 148—150° (decomp.), with dry hydrogen chloride, and *α-benzoylamino*isobutyrylglycine, $NHBz\cdot CMe_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 191°, by heating with glycine at 140—170°.

*Ethyl α-benzoylamino*isobutyrate has m. p. 123°, and the *methyl* ester, m. p. 124°. C. S.

Condensation of *p*-Hydroxybenzoic Acid with Formaldehyde. Felix Epstein (*J. pr. Chem.*, 1910, [ii], 81, 85—93).—The interaction of *p*-hydroxybenzoic acid, 40% formaldehyde, and dilute hydrochloric acid for eight to ten hours on the water-bath results in the formation of 2 : 2′-*dihydroxydiphenylmethane*-5 : 5-*dicarboxylic acid*, $[CO_2H\cdot C_6H_3(OH)]_2CH_2$, an ill-defined substance which carbonises by heating and does not yield crystalline derivatives ; the *copper* salt, $C_{15}H_{10}O_6Cu,3H_2O$, and the *diacetyl* derivative, $C_{19}H_{16}O_8$, have been prepared. By prolonged heating with concentrated sulphuric acid, it is converted into a green *sulphoxanthinedicarboxylic acid*, $C_{15}H_{10}O_8S$, which forms a green *copper* salt, $(C_{15}H_7O_8S)_2Cu_3$. C. S.

New Method of Preparing Ellagic Acid. L. V. Buschueff (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1484—1488).—The action of Berthollet's salt and hydrochloric acid on protocatechuic acid yields katellagic acid, whilst gallic acid under the same treatment gives ellagic acid. T. H. P.

Preparation of Acids and Amides from Phenyl Alkyl Ketones by means of Yellow Ammonium Sulphide. Conrad Willgerodt and Wilhelm Hambrecht (*J. pr. Chem.*, 1910, [ii], 81, 74—85).—The behaviour of *p*-tolyl alkyl ketones is exactly analogous to that of phenyl alkyl ketones in the reaction described previously (Abstr., 1909, i, 716) provided the conditions therein mentioned are strictly adhered to. The yields of amide and acid are less the greater the carbon content of the alkyl groups, and the preparation of fatty

aromatic acids by means of Willgerodt's reaction reaches its limit between the valeryl and the heptyl ketones.

p-Tolyl methyl ketone and yellow ammonium sulphide at 220° give 45% of *p*-tolylacetamide and 8—10% of *p*-tolylacetic acid, whilst with colourless ammonium sulphide, 2 : 5-di-*p*-tolylthiophen and 2 : 4-di-*p*-tolylthiophen are obtained in addition to the preceding amide and acid. Similarly, *p*-tolyl ethyl ketone and yellow ammonium sulphide at 210° yield 30% of *p*-tolylpropionamide and 6—8% of the corresponding acid. p-*Tolyl propyl ketone*, $C_7H_7\cdot COPr^a$, b. p. 247—248°, prepared from butyryl chloride and toluene in carbon disulphide in the presence of aluminium chloride, forms a *phenylhydrazone*, m. p. 73°, and by the Willgerodt reaction at 210° yields 18—20% of p-*tolylbutyramide*, m. p. 135°, and 5% of p-*tolylbutyric acid*, m. p. 60°, of which the *barium* and *silver* salts are described. *p*-Tolyl *iso*propyl ketone and yellow ammonium sulphide at 200° yield p-*tolyl*iso*butyramide*, m. p. 130°, and a very small amount of p-*tolyl*iso*butyric acid*, m. p. 85°. p-*Tolyl* iso*butyl ketone*, $C_7H_7\cdot CO\cdot CH_2\cdot CHMe_2$, b. p. 254—255°, obtained from toluene and *iso*valeryl chloride, forms an *oxime*, m. p. 65°, and yields 3—4% of p-*tolyl*iso*valeramide*, m. p. 150°, and a very slight trace of the *acid*, m. p. 128°, in the Willgerodt reaction at 190°. p-*Tolyl butyl ketone*, m. p. 17°, b. p. 261°, and yellow ammonium sulphide at 180° yield 2% of p-*tolylvaleramide*, m. p. 113°, and an unappreciable quantity of the corresponding acid. C. S.

Preparation of Benzophenoneimine Derivatives. G. Reddelien (*Ber.*, 1909, 42, 4759—4762).—A good yield of benzophenonephenylimine (diphenylmethyleneaniline; Pauly, this Journ., 1877, ii, 614; Graebe, Abstr., 1899, i, 702; Nägeli, *ibid.*, i, 910) can be prepared by condensing aniline and benzophenone with anhydrous zinc chloride at 160—180° for half an hour. Substituted anilines can react in a similar manner, and the stability of the product increases with the presence of negative substituents.

Diphenylmethylene-p-*toluidine*, $CPh_2{:}N\cdot C_6H_4Me$, is a viscid oil, and has b. p. 228°/15 mm., 245°/30 mm., or 360°/atm. pres.

The isomeric *meta*-derivative crystallises in rectangular, pointed prisms, m. p. 82·5°.

Diphenylmethylene-3 : 4-*xylidine*, $CPh_2{:}N\cdot C_6H_3Me_2$, forms rhombic plates, m. p. 122°.

Diphenylmethylene-m-*nitroaniline*, $CPh_2{:}N\cdot C_6H_4\cdot NO_2$, crystallises in yellow cubes or hexagonal plates, m. p. 123·5°. *Diphenylmethylene*-p-*aminophenol*, $CPh_2{:}N\cdot C_6H_4\cdot OH,C_2H_5\cdot OH$, forms yellow plates, m. p. 172°, and loses its alcohol of crystallisation at 110°. It is stable towards hydrolysing agents.

Diphenylmethylenedimethyl-p-*phenylenediamine*, $CPh_2{:}N\cdot C_6H_4\cdot NMe_2$, forms compact, orange-yellow crystals, and melts at 85° to a turbid, brown liquid, which clarifies at 93°.

A by-product, obtained in the preparation of the aniline derivative, is the zinc compound, $2NH_2Ph,ZnCl_2,2H_2O$ (Lachowicz and Bandrowski, Abstr., 1888, 1281). J. J. S.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. V. Nature of the Linking of the Halogen Atoms in the Ketohalides of Unsaturated Ketones. I. Fritz Straus [and, in part, A. Ackermann and Georg Lutz] (*Annalen*, 1909, 370, 315—367. Compare Straus and Ecker, Abstr., 1906, i, 859; Straus and Caspari, Abstr., 1907, i, 609; Straus and Ackermann, Abstr., 1909, i, 489; Straus and Hüssy, Abstr., 1909, i, 490).—The present communication deals mainly with the difference in the reactivity of the halogens in distyrylchlorobromomethane and *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane. These substances, prepared by the action of acetyl bromide or hydrogen bromide and calcium bromide on the corresponding chloro-carbinols dissolved in benzene, are distinctly yellow, a further example of the analogy between these ketohalides and triphenylmethyl halides.

The chlorobromides are strictly analogous with the corresponding keto-chlorides in their chemical properties; for example, the power of one of the ethylene linkings to add on halogen is completely lost; the benzylideneacetophenone derivative does not combine with bromine, and distyrylchlorobromomethane combines only with 1 mol. of bromine; further, the group >CClBr reacts in all cases so that only one atomic proportion of the halogen takes part in the change; thus, one mol. of the chlorobromide when acted on by water or methyl alcohol yields one mol. of hydrogen halide, about 96% of which is hydrogen bromide, the remainder being hydrogen chloride; similarly, an equivalent of halogen is eliminated from *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane when treated with an excess of silver oxide; the product is a mixture of the corresponding chlorocarbinol (about 98%) and bromocarbinol.

The rate at which the halogen in triphenylbromomethane, distyrylchlorobromomethane, diphenyldibromomethane, *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane, and the corresponding chloro-compounds is replaced by hydroxyl (compare Straus and Hüssy, *loc. cit.*) has been investigated; it is found that the reaction velocity decreases in the order given, and that the bromo-compounds are decomposed far more rapidly than the corresponding chloro-compounds.

The chlorobromides dissolve in concentrated sulphuric acid with the elimination of hydrogen halide; the reddish-violet solutions probably contain complex salts of the two sulphates, $RR_1CCl\cdot SO_4H$ and $RR_1CBr\cdot SO_4H$, with sulphuric acid; in support of this assumption it is found that the absorption spectra of the solutions differ slightly from those of the corresponding keto-chlorides. The solutions of the chlorobromides in liquid sulphur dioxide are more intensely coloured than those of the keto-chlorides, indicating a greater degree of ionisation, which probably takes place in two directions, $RR_1CCl \mid Br$ and $RR_1CBr \mid Cl$, but mainly in the manner indicated by the first formula.

Triphenylchloromethane when acted on by a *N*/4-solution of hydrogen bromide in benzene is converted into the corresponding bromo-compound to the extent of about 85%; the reaction is a reversible one, a state of equilibrium being reached in about five minutes. Similarly, the chlorine is largely replaced by bromine when

a solution of the chloro-compound in benzene is shaken with calcium bromide; this reaction is likewise reversible. The interaction of keto-chlorides with hydrogen bromide and with calcium bromide is of a more complex character; a solution of distyryldichloromethane in benzene containing hydrogen bromide is found to contain part of this substance in equilibrium with the corresponding chloro-bromide and di-bromide, as represented by the equation: $(CHPh{:}CH)_2CCl_2 + 2HBr \rightleftarrows (CHPh{:}CH)_2CClBr + HBr + HCl \rightleftarrows (CHPh{:}CH)_2CBr_2 + 2HCl$. Calcium bromide is found to react in a similar manner. On the other hand, when a solution of distyrylchlorobromomethane in benzene is treated with a slight excess of silver chloride, it is converted completely into the corresponding keto-chloride; this is in complete accord with the behaviour of triphenylbromomethane towards silver chloride.

The investigation has been extended to a study of the behaviour of tertiary butyl chloride and the corresponding bromide towards water, hydrogen halides, and calcium halides. It is found that these compounds are decomposed rapidly by water, and undergo reversible double decomposition when treated with a dissimilar hydrogen halide; the bromide interacts to a small extent with calcium chloride, but the chloride is not attacked by calcium bromide.

The different reactivity of the halogen atoms in the keto-chlorides and chloro-bromides is regarded by the author as due to a different form of union between the carbon atom and the two halogen atoms, the replaceable halogen being joined to the carbon by an ionogenetic valency ("*ionogene Valenz*"); accordingly, the bromo-chlorides and keto-chlorides are to be regarded as solid solutions of two valency isomerides in a state of equilibrium; this may be represented in the case of distyrylchlorobromomethane thus: $(CHPh{:}CH)_2CCl\sim\sim Br \rightleftarrows (CHPh{:}CH)_2CBr\sim\sim Cl$.

The bearing of the results obtained in this investigation on the question of the constitution of the triphenylhalogenmethanes is discussed, and the views of Baeyer (Abstr., 1909, i, 641) and Gomberg (Abstr., 1907, i, 504; 1909, i, 144) adversely criticised.

p-*Chlorophenyl*-p-*chlorostyrylchlorobromomethane*, $C_{15}H_{10}Cl_3Br$, crystallises in compact, pale yellow prisms, m. p. 98·5—99·5°; dilute solutions in liquid sulphur dioxide are violet-red, more concentrated solutions are pale yellow; a solution of the substance with stannic chloride in nitrobenzene is bluish-red.

Distyrylchlorobromomethane, $C_{17}H_{14}ClBr$, crystallises in stellate groups of large, slender, glistening, yellow leaflets, m. p. 91—92°; the *dibromide*, $C_{17}H_{14}ClBr_3$, crystallises in radially-grouped, colourless prisms and decomposes at 165—166°; the *mercuribromide*, $C_{17}H_{14}ClBr,4HgBr_2$, is a crystalline, green powder. W. H. G.

The Pyrogenetic Decomposition of (1) β-Benzopinacolin and (2) α-Benzopinacolin. Maurice Delacre (*Bull. Soc. chim.*, 1909, [iv], 5, 1144—1149, 1149—1153).—Both products were first carefully purified and then heated in retorts, the products of distillation being collected and separated by fractional distillation, and finally by crystallisation from appropriate solvents, where necessary. Full details of these separations are given in the original papers.

β-Benzopinacolin yielded triphenylmethane, *p*-benzoyltriphenylmethane, tetraphenylethylene, "needles," benzene, benzaldehyde, benzophenone, and unidentified products boiling at 240—320°, 340—430°, and 405—440°, and some carbonaceous residue.

α-Benzopinacolin furnished substantially the same products, with the addition of "yellow needles" and unidentified products of somewhat different boiling points. The relative yields of the various substances were not the same in the two cases. An unidentified substance, showing violet fluorescence, was present in both sets of distillation products. The "needles" were isolated from the fractions boiling at 325—380° and 380—405; this material had m. p. 144°, and may be identical with Hemilian's hydrocarbon, $C_{19}H_{14}$. The "yellow needles" obtained from α-benzopinacolin came from the same fractions as the "needles"; this product had m. p. 245°, and contained carbon, 78·8%, and hydrogen, 4·5%. T. A. H.

Action of Acetic Anhydride on Octabromo-1′-hydroxy-1-methoxy-*o*-quino-1-monoxide. C. Loring Jackson and H. A. Flint (*Amer. Chem. J.*, 1910, **43**, 7—11).—Jackson and Porter (Abstr., 1904, i, 254) and Jackson and Carlton (Abstr., 1905, i, 907) have shown that tetrabromo-*o*-quinone readily unites with methyl alcohol to form a compound, termed the methyl α-compound, which, when boiled with methyl alcohol, is converted into an isomeric or β-compound. Jackson and MacLaurin (Abstr., 1907, i, 223) have found that the α-compound is octabromo-1′-hydroxy-1-methoxy-*o*-quino-1-monoxide, and that the β-compound is octabromo-1′-hydroxy-1-methoxy-*o*-quino-1 : 2 : 2-trioxide. These authors also found that by the action of acetic anhydride on the α-compound, two substances were produced, one of which was yellow and had m. p. 225°, whilst the other was white and had m. p. 218°.

A further study of the yellow compound has shown that, when pure, it has m. p. 244° (decomp.), and that it is identical with heptabromo-*o*-quinocatechol hemi-ether (Jackson and Russe, Abstr., 1906, i, 288). On treating this substance with hot acetic anhydride, it is converted into hexabromo-*o*-quinocatechol ether (Jackson and Koch, Abstr., 1901, i, 597). When heptabromo-*o*-quinocatechol hemi-ether is shaken with 10% solution of sodium hydroxide, a *substance*, m. p. about 240° (decomp.), is obtained, which forms white, rhombic crystals. E. G.

Aminoanilide and Certain New Dianilides of α-Naphthaquinone. Oswald Miller and J. Smirnoff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1420—1421). — In acetic acid solution, amino-imino-α-naphthaquinone (di-iminonaphthol) hydrochloride is converted by aromatic amines into the corresponding dianilides :

$$C_6H_4\begin{<}\begin{matrix}CO\text{——}C\cdot NH_2\\ \|\quad\quad\|\\ C(NH)\cdot CH\end{matrix}\end{>} + 2NH_2Ph = 2NH_3 + C_6H_4\begin{<}\begin{matrix}CO\text{——}C\cdot NHPh\\ \|\quad\quad\|\\ C(NPh)\cdot CH\end{matrix}\end{>}.$$

The reaction probably takes place in two stages, the first of these resulting in the formation of an aminoanilide of α-naphthaquinone, $C_6H_4\begin{<}\begin{matrix}CO\text{——}C\cdot NH_2\\ \|\quad\quad\|\\ C(NR)\cdot CH\end{matrix}\end{>}$. The authors find that these intermediate aminoanilides, which have not been described previously, are obtained

when the reaction between the aromatic amine and the di-iminonaphthol hydrochloride takes place in alcoholic solution, in which the velocity of formation of dianilide from aminoanilide is less than that of the aminoanilide itself.

The aminoanilides of α-naphthaquinone are coloured, crystalline compounds, readily soluble in alcohol or dilute acid; in most cases they exhibit softening before melting. The following compounds of this type have been obtained in the pure state.

Aminoanilide, brown prisms or red needles, m. p. 121°. *Amino-o-toluidide*, red needles, m. p. 115°. *Amino-m-toluidide*, red needles, m. p. 110°. *Amino-p-toluidide*, red needles, m. p. 122·5°. *Amino-xylidide* (Me : Me : NH_2 = 1 : 2 : 4), red prisms or needles, m. p. 144°. *Amino-xylidide* (Me : Me : NH_2 = 1 : 3 : 4), pale red prisms or needles, m. p. 160°. *Amino-xylidide* (Me : Me : NH_2 = 1 : 4 : 5), reddish-brown needles, m. p. 153°. *Amino-ψ-cumidide*, red needles, m. p. 155°.

The following new dianilides of α naphthaquinone have also been prepared. *Di-o-toluidide*, orange prisms or needles, m. p. 123·5°. *Di-m-toluidide*, red needles, m. p. 147°. *Dixylidide* (1 : 2 : 4), reddish-brown prisms or needles, m. p. 184°. *Dixylidide* (1 : 3 : 4), reddish-brown prisms, m. p. 154° (?). *Dixylidide* (1 : 4 : 5), reddish-brown prisms or needles, m. p. 114° (?). T. H. P.

Action of Piperidine on *d*-Pinene Chloro-oxime. L. V. Buschueff (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1481—1484).—The action of piperidine on the chloro-oxime of *d*-pinene isolated from Russian turpentine yields (1) nitrosopinene, agreeing in all its properties with that obtained by Golubeff (Abstr., 1908, i, 902) from the *l*-pinene of the ethereal oil of the Siberian fir; (2) pinene nitrolpiperidine (compare Wallach, Abstr., 1888, 1098). T. H. P.

Conversion of Pulegone into Menthenes. Karl Auwers (*Ber.*, 1909, 42, 4895—4907).—3-Chloro*iso*terpinolene (from pulegone), when reduced with sodium and amyl alcohol, yields, not the expected *iso*terpinolene, but a mixture of Δ^3- and $\Delta^{4(8)}$-menthene. Hence this reduction forms an exception to the general rule regarding the addition of hydrogen to conjugated double linkings. R. V. S.

Matico Leaves and Matico Oils. Hermann Thoms (*Arch. Pharm.*, 1909, 247, 591—612).—Commercial matico oils rarely have the same or a similar composition, because they are prepared from various kinds of *Piper*, the constituents of which vary considerably. The author has prepared and examined matico oils from botanically individual leaf-material. Japan camphor and borneol, hitherto undetected in matico oils, have been discovered in the oil from *Piper camphoriferum*. On the contrary, cineol, parsley apiole, asarone, and matico camphor, which have frequently been found in commercial oils, could not be detected by the author in his oils. Dillapiole is present in particularly large amount in the oil from the leaves of *Piper acutifolium* var. *subverbascifolium*. C. S.

The Essential Oil of Hyacinths. C. J. Enklaar (*Chem. Weekblad*, 1910, 7, 1—11).—When distilled at 10 mm. pressure, the

essential oil of hyacinths yields three fractions, distilling respectively below 90°, at 92—94°, and between 94° and 150°. The first fraction contains a very volatile substance of disagreeable odour. When evaporated over concentrated sulphuric acid, it develops a red colour. The second fraction contains an unknown *substance* of powerful odour, its formula being probably $C_{15}H_{20}O$. It has b. p. 205—206°/760 mm., D^{15} 0·907, n_D^{16} 1·4914, and forms 50% of the oil. The third fraction contains benzyl benzoate and other esters (20% of the oil), an unknown fluorescent substance which is free from nitrogen (5%), and benzyl alcohol with other primary alcohols (1%). A. J. W.

Decomposition of Amygdalin. Karl Feist (*Arch. Pharm.*, 1909, 247, 542—545. Compare Abstr., 1909, i, 589).—The synthetic production of *d*-benzaldehydecyanohydrin by the action of emulsin on benzaldehyde and hydrogen cyanide is a more rapid process, according to Auld (Trans., 1909, 95, 927), than its formation by the decomposition of amygdalin by emulsin, thus indicating that its formation in the latter reaction is due to a secondary and not to a primary reaction. Since these results are exactly the reverse of those obtained previously by the author, he has repeated his experiments without adding dextrose, and confirms Auld's results. The emulsin used was obtained from Kahlbaum, that in the former experiments from Schuchardt. Since Rosenthaler (Abstr., 1908, i, 817) has shown that emulsin contains a hydrolysing and also a synthesising enzyme, the discrepancy between the author's two series of experiments is attributed to the fact that Kahlbaum's emulsin contains a preponderance of the synthesising enzyme, and Schuchardt's of the hydrolysing enzyme.

The author still maintains, however, that *d*-benzaldehydecyanohydrin is a primary product of the decomposition of amygdalin by emulsin, because emulsin, freed from the synthesising enzyme by Rosenthaler's method (Abstr., 1909, i, 622), acting on amygdalin and also on a mixture of benzaldehyde and hydrogen cyanide, produces in the former case a slightly dextrorotatory solution, whilst in the latter the solution remains inactive. Moreover, Walker and Krieble have shown that the decomposition of amygdalin by sulphuric acid yields dextrose and benzaldehydecyanohydrin (Trans., 1909, 95, 1369), and the author finds that when amygdalin is treated with 2·77*N*-sulphuric acid for three hours at 98° and extracted with benzene, the solution, although dark coloured, is distinctly dextrorotatory. C. S.

Crystalline Chitosan Sulphate. Emil Löwy (*Biochem. Zeitsch.*, 1909, 23, 47—60).—The chitosan was prepared from the shells of *Nephrops norvegicus*, from the chitin of which the chitosan was obtained by heating at 170—180° with potassium hydroxide. The hydrochloride, hydrobromide, and sulphate were prepared by allowing hot solutions of the chitosan in the respective acids to cool. The concentration of the acids must be fairly high, as the chitosan is readily soluble in dilute acids. The salts were obtained crystalline. The analyses of the sulphate correspond with the formula

$$C_{28}H_{50}O_{19}N_4(H_2SO_4)_3.$$

It can form additive products with bromine and iodine, taking up the

halogen in the proportion of one chlorine or bromine atom to two of nitrogen. It yields on hydrolysis (the products of which were quantitatively estimated) glucosamine and acetic acid, and it is assumed that the chitosan is a polymeric form of monoacetyldiglucosamine, and that the hydrolysis can be represented by the equation: $(C_{28}H_{50}O_{19}N_4)_x + 5xH_2O = 4x(C_6H_{13}O_5N) + 2x(CH_3\cdot CO_2H)$.

S. B. S.

Formation of Phlobaphens. Maximilian Nierenstein and T. A. Webster (*Collegium*, 1909, 337—341).—Mangrove tannin is oxidised by oxygen, hydrogen peroxide, or potassium persulphate solution, yielding phlobaphens. The phlobaphen formed when oxygen is used, gave anthracene when distilled with zinc dust (compare Abstr., 1908, i, 40). The hydrogen peroxide oxidation product gave diphenylmethane when distilled with zinc, and the phlobaphen obtained by oxidising the tannin with an acetic acid solution of potassium persulphate in the presence of sulphuric acid, gave anthracene when distilled with zinc dust. The latter compound is termed *β-phlobaphen*, and the product which yields diphenylmethane, *α-phlobaphen*. The *α*-compound when boiled with dilute sulphuric acid yields the *β*-derivative. It is probable that this conversion is accompanied by the elimination of water and the formation of an anthraquinone skeleton.

J. J. S.

Constituents of the Rhizome of Imperatoria. Johannes Herzog and D. Krohn (*Arch. Pharm.*, 1909, 247, 553—591).—The paper deals with a comparative examination of the crystalline constituents of the rhizomes of *Imperatoria* and *Peucedanum*. Earlier workers have shown that the latter contains peucedanin and oxypeucedanin (Schmidt, Abstr., 1899, i, 377), whilst the former contains ostruthin, oxypeucedanin, but not peucedanin (Gorup-Besanez, Abstr., 1874, 907; 1877, 717; Jassoy, Abstr., 1890, 1154). Oxypeucedanin has only once been found in the rhizome of *Imperatoria* (Heut, Abstr., 1875, 772), and then in such small amount that its identity with the oxypeucedanin of *Peucedanum* has not been certainly established.

Using their former method (Abstr., 1908, ii, 978), the authors extract the rhizomes of *Imperatoria* with boiling benzene, concentrate the extract, and treat it with light petroleum, whereby a viscous mass is separated which soon becomes crystalline. The mass is treated with ether, and the oxypeucedanin thus obtained is recrystallised successively from acetone, alcohol, and chloroform, and then has m. p. 142—142·5°; the mother liquor after fourteen days has deposited a new substance, *ostruthol*, m. p. 134—134·5°, which depresses the m. p. of oxypeucedanin and does not form an additive compound with hydrogen chloride. The benzene-light petroleum solution contains another new substance, *osthol*, m. p. 83—84°, and ostruthin. The last-mentioned substance is better isolated from the rhizome by the alcohol method recommended by Gorup-Besanez and Jassoy.

The percentage yields of these substances are: oxypeucedanin, 1·3; ostruthol, 0·3; osthol, 0·1; ostruthin, 0·5. Young two-year old rhizomes of *Peucedanum*, extracted by the benzene process, yield 2%

of peucedanin and 0·3% of oxypeucedanin, whilst old roots yield 2·5 and 0·5% respectively of the two substances. These figures refute the current view of the formation of the oxypeucedanin, for since the percentage of both peucedanin and oxypeucedanin in old rhizomes is greater than in young roots, the latter cannot be produced by oxidation at the expense of the former. The oxypeucedanin from *Imperatoria* is shown to be identical with that from *Peucedanum* by a mixed m. p. determination and by a comparison of the hydrogen chloride additive compounds.

Being able to obtain oxypeucedanin in comparatively large quantities, the authors have examined its properties more fully than previous investigators. It is optically inactive, and has m. p. 142—142·5°. The analytical data point to the formula $C_{13}H_{12}O_4$, which is confirmed by a determination of the molecular weight in glacial acetic acid and in benzene by the ebullioscopic method. By passing hydrogen chloride into a concentrated alcoholic solution at 0° and then slowly adding a large amount of water, a white, crystalline *substance*, m. p. 155·5—157°, is obtained, the analysis of which points to the formula $C_{36}H_{34}O_{11}Cl_2$, but the authors regard the substance as an additive compound of $C_{13}H_{12}O_4$, the discrepancy being attributed to the ready loss of hydrogen chloride. Boiling 10% sulphuric acid changes oxypeucedanin into an isomeric *substance*, $C_{13}H_{12}O_4$, m. p. 144—145·5°, which does not form an additive compound with hydrogen chloride. By treating oxypeucedanin with boiling 1% oxalic acid, a hydrated *product*, $C_{13}H_{14}O_5$, m. p. 132—133°, is obtained, which forms yellow crystals, and has a molecular weight in boiling glacial acetic acid corresponding with its formula. It readily loses water by treatment with 38% hydrochloric acid, yielding the isomeride of oxypeucedanin, m. p. 144—145·5°, which is also produced by the action of zinc and boiling acetic acid on the hydrogen chloride additive compound of oxypeucedanin. The hydrated product forms a yellow acetyl *derivative*, $C_{15}H_{16}O_6$, m. p. 155·5—156·5°, and a *phenylurethane*, $C_{20}H_{19}O_6N$, m. p. 170—170·5°, from both of which the hydrated product can be regenerated by the action of alcoholic potassium hydroxide and alcoholic ammonia respectively. Oxypeucedanin in acetone is reduced by aluminium amalgam, yielding a mixture which is separable by alcohol; the less soluble constituent, m. p. 203—205°, has a molecular weight in boiling acetic acid corresponding with the formula $(C_{13}H_{13}O_4)_2$, a result suggesting that oxypeucedanin is an unsaturated lactone. This conception is supported by the behaviour of oxypeucedanin with alkali hydroxides; with excess of alkali, it gives in aqueous-alcoholic solution yellow salts, which decompose at the ordinary temperature in neutral or faintly alkaline solution.

The authors confirm Jassoy's formula, $C_{18}H_{20}O_3$, for ostruthin by analysis, by titration with acid and alkali, and by a Zeisel estimation of the *ester*, $C_{18}H_{19}O_3{\cdot}CO_2Me$, m. p. 64—65°, obtained by the interaction of methyl chloroformate and a strongly cooled solution of an alkali salt of ostruthin.

Osthol, $C_{15}H_{16}O_3$, m. p. 83—84°, forms long, white crystals, and contains one methoxy-group. In alcoholic solution, it yields with

hydrogen chloride an additive *compound*, $C_{15}H_{16}O_3,HCl$, m. p. 99·5—100°. In aqueous alcohol, it behaves with alkali hydroxides very much like oxypeucedanin, its salts in neutral or faintly alkaline solution decomposing into free alkali and osthol, which, therefore, is probably a lactone.

Osthruthol crystallises in white needles, m. p. 134—134·5°, and from the analytical data and the determination of its molecular weight in boiling benzene or methyl alcohol, has the composition $(C_3H_3O)_8$. Its behaviour with alkali hydroxides is similar to that of oxypeucedanin and osthol, the yellow solutions of the salts being decomposed by carbon dioxide. Osthruthol is probably a lactone. C. S.

Rhein. Otto A. Oesterle and G. Riat (*Arch. Pharm.*, 1909, 247, 527—534).—Rhein, the formula of which now appears to be established beyond doubt as $C_{15}H_8O_6$, yields a dark red, crystalline *potassium* derivative, $C_{15}H_6O_6K_2,9H_2O$, and a *propionate*,

$$C_{15}H_6O_4(O\cdot CO\cdot CH_2\cdot CH_3)_2,$$

m. p. 223—224°.

Farbwerke vorm. Meister, Lucius und Brüning (D.R.-P. 158277) have shown that ethyl chloroacetate reacts easily with anthraquinone derivatives containing hydroxyl groups in the β-position, yielding ethers of ethyl glycollate. When the potassium derivative of rhein is boiled from seventeen to eighteen hours with ethyl chloroacetate, a golden-yellow, crystalline *substance*, $C_{23}H_{20}O_{10}$, m. p. 153—154°, is obtained, containing two ethyl glycollate residues. Since, however, the substance yields an *acetyl* derivative, m. p. 179—180°, in the usual way, the ethyl glycollate groups cannot have entered both the phenolic hydroxyl groups in rhein: one must be present in a hydroxyl group in a side-chain. The authors were proving that this hydroxyl group is present as a carboxyl group when Robinson and Simonsen's paper appeared (Trans., 1909, 95, 1085), in which rhein is shown to be a dihydroxyanthraquinonecarboxylic acid. The behaviour of rhein with ethyl chloroacetate is in accordance with the probability that rhein is a derivative of chrysazin (Abstr., 1909, i, 946). C. S.

Chlorophyll. VIII. Degradation of Chlorophyll by Alkalis. Richard Willstätter and Hermann Fritzsche (*Annalen*, 1910, 371, 33—124. Compare this vol., ii, 150).—The present investigation on the products formed successively by the action of alkalis on chlorophyll is mainly an amplification of the work of Willstätter and Pfannenstiel on rhodophyllin (compare Abstr., 1908, i, 198). The chlorophylls are derivatives of a tricarboxylic acid; crystalline chlorophyll contains two carbmethoxy-groups, whilst the amorphous compound contains only one carbmethoxy-group and one phytol residue. Crystalline chlorophyll, when hydrolysed, yields a tricarboxylic acid (chlorophyllin), which is acted on by methyl sulphate, yielding the corresponding trimethyl ester, a substance far more soluble than chlorophyll and very similar in composition and properties to the compound formed by the prolonged action of methyl alcohol on chlorophyll. Amorphous chlorophyll, which cannot be obtained

entirely free from impurities, when hydrolysed and subsequently methylated yields a trimethyl ester identical with that derived from crystalline chlorophyll; this ester when treated with potassium hydroxide is converted into the potassium salt of chlorophyllin, identical with the salt prepared directly from crystalline chlorophyll. The various preparations of the trimethyl ester contain two distinct substances: a blue compound and a green compound soluble with difficulty, which are separated by fractional precipitation and are similar in composition.

The action of alkalis on chlorophyll at 100—200° leads to the formation of two dicarboxylic acids, glaucophyllin and rhodophyllin, which are very similar both in chemical and physical properties, and can be separated only by the difference in their acidic properties.

The formation of rhodophyllin at 200° is accompanied by that of a monocarboxylic acid, phyllophyllin, whilst a second monocarboxylic acid, pyrrophyllin, is formed at 225—240°; the two compounds just mentioned are extremely similar, both chemically and optically; phyllophyllin is distinguished, however, by the solubility of the alkali and alkaline earth salts in ether. The monocarboxylic acids are less acidic than the dicarboxylic acids; thus, rhodophyllin may be separated from them by means of dilute ammonium hydroxide, in which phyllophyllin and pyrrophyllin are insoluble.

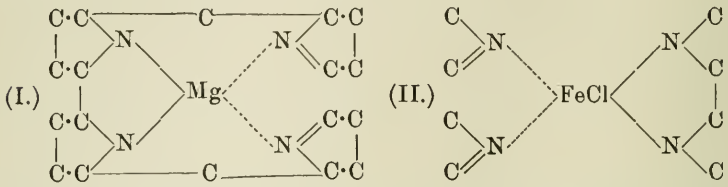
The phyllins are converted by acids into the corresponding porphyrins, compounds which do not contain magnesium. In order to emphasise this relationship between phyllins and porphyrins, it is proposed to change the name of the compound derived from rhodophyllin from *allo*porphyrin into rhodoporphyrin (compare Willstätter and Pfannenstiel, *loc. cit.*).

The dicarboxylic acids, glaucoporphyrin and rhodoporphyrin, are well-defined, crystalline compounds, soluble with difficulty and extremely similar in chemical properties; rhodoporphyrin is not identical with Tschirch's phyllopurpuric acid, as suggested by Marchlewski (compare Abstr., 1908, i, 357). The monocarboxylic porphyrins, phylloporphyrin and pyrroporphyrin, resemble one another so closely that it is difficult to decide which of them corresponds with the substance described hitherto as phylloporphyrin, although it is very probable that the more basic of the two compounds (phylloporphyrin) is identical with the phylloporphyrin described by Marchlewski recently (*loc. cit.*); the phylloporphyrin of previous investigators was undoubtedly contaminated with other porphyrins.

The analysis of the complex substances described in this paper is rendered difficult owing to the stability of the compounds which they form with ether; however, from the results obtained it appears that the complex $[C_{31}H_{34}N_4Mg]$ is common to the phyllins, one, two, and three atoms of hydrogen being replaced by carboxyl in pyrrophyllin and phyllophyllin, glaucophyllin and rhodophyllin, chlorophyll, and the chlorophyllins respectively. The porphyrins are derived from the common nucleus $[C_{31}H_{36}N_4]$ in a similar manner.

As a result of the study of the phyllin esters and salts, particularly of those containing only one carboxyl group, it follows that carboxyl does not take part in the formation of the complex in the derivatives

of chlorophyll, and that only the groups containing nitrogen are available for attachment to the magnesium atom; the centre of the complex may be represented by (I). Applying the same arguments in the case of hæmin, it follows that the iron in hæmin derivatives is combined in the manner indicated by (II) (compare Piloty and Merzbacher, Abstr., 1909, *i*, 857):



I. Phyllins.—Potassium chlorophyllin is a bluish-green powder, analyses of which indicate the atomic proportions N_4:0·90Mg:2·60K; when treated with methyl sulphate, it yields a mixture of two *chlorophyllin trimethyl* esters; the more soluble ester is a bluish-black, microscopic, crystalline powder, whilst the less soluble is a pale green powder. Both esters are decomposed by oxalic acid with the elimination of magnesium and formation of crystalline products containing oxalate; the solutions of the derivatives from the green and blue esters in chloroform are olive-brown and olive-green respectively.

Glaucophyllin, $C_{33}H_{34}O_4N_4Mg$, prepared by the action of a concentrated methyl-alcoholic solution of potassium hydroxide on chlorophyllin under pressure at a temperature not exceeding 140°, is purified by extracting the ethereal solution of the crude material with 0·004% ammonia, treating the aqueous solution with sodium dihydrogen phosphate, extracting with ether, and shaking the ethereal solution with a 0·02—0·05% solution of disodium hydrogen phosphate, in which glaucophyllin is insoluble; it crystallises in small, glistening prisms, which are green by transmitted light and greyish-blue by reflected light, and forms violet-blue solutions with an intense red fluorescence; the *potassium* salt, $C_{31}H_{32}N_4Mg(CO_2K)_2$, crystallises in microscopic, slender, violet prisms. Glaucophyllin is converted by alcoholic potassium hydroxide under pressure at 195—200° into rhodophyllin.

Rhodophyllin forms a complex *potassium* salt,

$$C_{33}H_{32}O_4N_4MgK_2,KOEt;$$

the normal potassium salt when treated with methyl sulphate yields the *dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, which crystallises in glistening prisms with a violet reflex and sinters at 310°.

Pyrrophyllin, $C_{32}H_{34}O_2N_4Mg$, is best prepared by the action of alcoholic potassium hydroxide on rhodophyllin under pressure at 225—230°; it crystallises in tufts of glistening plates, which are steel-blue or greyish-blue with a red tinge; recrystallisation from ether decreases the solubility of the compound without altering the composition; the ethereal solution at the same time changes from blue to red; the substance crystallises from absolute ether in glistening, reddish-violet prisms. The *pyridine* salt crystallises in glistening, violet leaflets; the *potassium* salt, $C_{31}H_{33}N_4Mg{\cdot}CO_2K$, crystallises in short, dark red prisms; the *calcium* salt, $(C_{32}H_{33}O_2N_4Mg)_2Ca$, forms

small, pale red needles; the *ammonium* salt forms brilliant red needles; the *sodium* salt crystallises in pale violet needles.

Phyllophyllin is formed in large quantity by the action of a methyl-alcoholic solution of potassium hydroxide on amorphous chlorophyll under pressure at 225—230°; it has not been isolated in a crystalline form, since it decomposes very readily; the ethereal solution is bluish-red with a red fluorescence; the *caesium* salt, $C_{31}H_{33}N_4Mg\cdot CO_2Cs$, crystallises in compact, glistening, bluish-violet prisms; the *potassium* salt ($1H_2O$) forms glistening, violet prisms; the *calcium* salt crystallises in bright red needles; the *magnesium* salt forms glistening, slender needles.

II. Porphyrins.—*Glaucoporphyrin*, $C_{33}H_{36}O_4N_4$, crystallises in reddish-violet, microscopic needles; it sinters at 270° and is completely decomposed at 290—295°; the *potassium* salt,

$$C_{31}H_{34}N_4(CO_2K)_2,4H_2O,$$

crystallises in slender, pale brown leaflets; the *complex salt* with zinc acetate crystallises in glistening, violet prisms.

Rhodoporphyrin forms with zinc acetate an *additive compound*, crystallising in red needles, and with ferric chloride in glacial acetic acid a complex *iron* compound, obtained as a greyish-black, crystalline powder; the *dimethyl* ester, $C_{31}H_{34}N_4(CO_2Me)_2$, crystallises in glistening, reddish-brown prisms with a coppery reflex.

Pyrroporphyrin, $C_{32}H_{36}O_2N_4$, crystallises in dark red, truncated prisms with a violet, metallic reflex; the solution in glacial acetic acid is red with a slight blue tinge. The *hydrochloride*, $C_{32}H_{36}O_2N_4,2HCl$, crystallises in brown, slender, pointed prisms; the *hydrochloride*, $C_{32}H_{36}O_2N_4,3HCl$, forms glistening, rhomboidal leaflets, which are brownish-red by transmitted light, violet by reflected light; the *potassium* salt, $C_{31}H_{35}N_4\cdot CO_2K$, crystallises in reddish-brown prisms and rhomboidal leaflets; the *magnesium* salt was analysed; the *methyl* ester, $C_{31}H_{35}N_4\cdot CO_2Me$, crystallises in long prisms; the *acetyl* compound, $C_{31}H_{35}N_4\cdot CO_2Ac$, prepared by the action of hot acetic anhydride on pyroporphyrin, crystallises in rhomboidal leaflets and long prisms, which are red by transmitted light.

Phylloporphyrin crystallises in dark red, pointed prisms with a violet, metallic reflex; the solution in glacial acetic acid is dark violet-red; the *hydrochloride*, $C_{32}H_{36}O_2N_4,3HCl$, crystallises in glistening, violet, four-sided prisms; the *magnesium* salt, $(C_{32}H_{35}O_2N_4)_2Mg$, is a brownish-red powder. The compound described by Schunck and Marchlewski as a zinc salt is a complex zinc compound.

The absorption spectra of alcoholic and ethereal solutions of glaucophyllin, pyrrophyllin, phyllophyllin, pyrroporphyrin, and phylloporphyrin, and of the hydrochlorides of the last two substances have been measured and are represented graphically. W. H. G.

The Tanning Process. Johann von Schroeder (*Kolloidchem. Beihefte*, 1909, 1, 1—57).—The quantity of tannic acid adsorbed by unit weight of hide-powder is approximately constant; the amount which can be washed out again is less the longer the two have remained in contact. Water plays a certain part in the process, for hide-powder takes up no tannin from an alcoholic solution. A preliminary

treatment of the powder with formaldehyde largely prevents the subsequent adsorption of tannic acid. Gelatin resembles hide-powder in its relationship to tannic acid, if due allowance is made for the differences of physical condition of the two former substances under the circumstances of the experiment. G. S. W.

Constitution of Hydroxymethylfurfuraldehyde. Jan J. Blanksma (*Chem. Weekblad*, 1909, 6, 1047—1053. Compare Kiermayer, Abstr., 1896, i, 144; Fenton and Robinson, Trans., 1909, 95, 1334).—Hydroxymethylfurfuraldehyde is formed by dehydration of chitose, and is the aldehyde, $\begin{matrix}CH{=}{=}C(COH)\\ |\\ CH{:}C(CH_2{\cdot}OH)\end{matrix}\!>\!O$, corresponding with 2-hydroxymethylfuran-5-carboxylic acid, not with 4-hydroxy-2-methylfuran-5-carboxylic acid, as supposed by Kiermayer. The small proportion of furfuraldehyde obtained by heating certain pentoses is attributed to the partial decomposition of the hydroxymethylfurfuraldehyde first formed. A. J. W.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. VIII. Ludwig Kaluza (*Monatsh.*, 1909, 30, 701—726. Compare Andreasch, Abstr., 1908, i, 683, 684).—Rhodanic acids have been prepared from *ψ*-cumidine and *iso*hexylamine.

3-*ψ-Cumylrhodanic acid*, $C_6H_2Me_3{\cdot}N\!<\!\begin{matrix}CS{-}S\\ |\\ CO{\cdot}CH_2\end{matrix}$, is obtained in the form of an oil from the corresponding ester, *ethyl ψ-cumyldithiocarbamacetate*, $C_6H_2Me_3{\cdot}NH{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2Et$, which is formed by the interaction of ethyl chloroacetate and ammonium cumyldithiocarbamate, and crystallises in short, transparent prisms, m. p. 84°.

5-*Benzylidene*-3-*ψ-cumylrhodanic acid*,

$$C_6H_2Me_3{\cdot}N\!<\!\begin{matrix}CS{-}S\\ |\\ CO{\cdot}C{:}CHPh\end{matrix}'$$

prepared by condensation with benzaldehyde, is a citron-yellow oil, crystallising in citron-yellow needles, m. p. 127°.

5-mp-*Methylenedioxybenzylidene*-3-*ψ-cumylrhodanic acid*, similarly prepared by condensation with piperonal, is a coarse, chrome-yellow powder, consisting of prismatic needles, m. p. 188°.

5-m-*Nitrobenzylidene*-3-*ψ-cumylrhodanic acid* forms a sulphur-yellow, crystalline powder, m. p. 224°. The corresponding 5-p-*nitrobenzylidene*-3-*ψ-cumylrhodanic acid* is a dark yellow powder, which becomes brown at 190°, sinters at 200°, m. p. 230°.

5-p-*Dimethylaminobenzylidene*-3-*ψ-cumylrhodanic acid* forms splendid blood-red, stout needles, m. p. 192°. The alcoholic solution is a deep chrome-yellow when dilute, blood-red when concentrated.

5-p-*Methoxybenzylidene*-3-*ψ-cumylrhodanic acid* forms glistening, chrome-yellow, microscopic prisms, m. p. 174°.

iso*Hexylamine* iso*hexyldithiocarbamate*, $C_6H_{13}{\cdot}NH{\cdot}CS{\cdot}S{\cdot}NH_3{\cdot}C_6H_{13}$, prepared by the interaction of *iso*hexylamine and carbon disulphide, forms colourless, regular, prismatic crystals, m. p. 85°. It reacts with ethyl monochloroacetate, forming 3-iso*hexylrhodanic acid*,

$$C_6H_{13}{\cdot}N\!<\!\begin{matrix}CS{-}S\\ |\\ CO{\cdot}CH_2\end{matrix}'$$

a clear, fluid, transparent, light yellow oil, b. p. 199—200°/11 mm.

5-*Benzylidene*-3-iso*hexylrhodanic acid*, $C_6H_{13}\cdot N<\begin{matrix}CS-S\\ |\\ CO\cdot C:CHPh\end{matrix}$, forms long, lustrous, bright yellow needles, m. p. 87°. 5-m-*Nitrobenzylidene*-3-iso*hexylrhodanic acid* crystallises in light yellow, glistening plates, m. p. 166—167°. 5-p-*Nitrobenzylidene*-3-iso*hexylrhodanic acid* is a brownish-yellow, microcrystalline powder, m. p. 130—131°.

5-mp-*Methylenedioxybenzylidene*-3-iso*hexylrhodanic acid*,

$$C_6H_{13}\cdot N<\begin{matrix}CS-S\\ |\\ CO\cdot C:CH\cdot C_6H_3<\begin{matrix}O\\ O\end{matrix}>CH_2\end{matrix},$$

consists of golden-yellow, lustrous needles with a blue reflex, m. p. 98°. 5-p-*Dimethylaminobenzylidene*-3-iso*hexylrhodanic acid* forms a matted mass of lustrous, red needles with a blue reflex, m. p. 140°. 5-o-*Hydroxybenzylidene*-3-iso*hexylrhodanic acid* crystallises in orange-yellow, short, matted needles, m. p. 170—172°. With sodium hydroxide, bluish-red crystals of the sodium salt are formed. It dyes wool and silk bright yellow.

5-p-*Methoxybenzylidene*-3-iso*hexylrhodanic acid* forms long, chrome-yellow, lustrous needles, m. p. 85°.

5-*Cinnamylene*-3-iso*hexylrhodanic acid* forms golden, crystalline masses, consisting of regular, rectangular, microscopic cubes, m. p. 129—131°.

iso*Hexylthiocarbimide*, $SC:N\cdot[CH_2]_3\cdot CHMe_2$, prepared by the interaction of ethyl chlorocarbamate and *iso*hexylamine *iso*hexyldithiocarbamate, is a faintly yellow-coloured, clear, mobile oil, with a not unpleasant odour, b. p. 120—121°/18 mm., 208—209°/760 mm. When treated with ammonia and alcohol, iso*hexylthiocarbamide*,

$$NH_2\cdot CS\cdot NH\cdot C_6H_{13},$$

is formed, crystallising in thin, rectangular plates, m. p. 62°, of fatty lustre. *Di*iso*hexylthiocarbamide*, $CS(NH\cdot C_6H_{13})_2$, forms thin, silvery-glistening, rhombic plates, m. p. 46°.

iso*Hexylthioparabanic acid*, $CS<\begin{matrix}N(C_6H_{13})\cdot CO\\ |\\ NH---CO\end{matrix}$, prepared by the interaction of *iso*hexylthiocarbamide and cyanogen, crystallises in light yellow, thin plates, m. p. 110°. By the action of silver nitrate it is converted into iso*hexylparabanic acid*, $CO<\begin{matrix}N(C_6H_{13})\cdot CO\\ |\\ NH---CO\end{matrix}$, which forms long, colourless, silky, matted needles, m. p. 76°. *Di*iso*hexylthioparabanic acid* crystallises in long, flat, citron-yellow needles, m. p. 40°. *Di*iso*hexylparabanic acid* was only obtained in the form of a syrup. E. F. A.

Additive Products of Halogen Acetamide with Atropine. Alfred Einhorn and Maximilian Göttler (*Ber.*, 1909, 42, 4853—4854).—The additive product of atropine with bromoacetonitrile has been shown by Braun (Abstr., 1908, i, 675) to have lost the specific pharmacological action of atropine; this is not, however, the case as regards the compounds with the halogen acetamides.

Atropinechloroacetamide forms a flocculent precipitate of lustrous

plates, m. p. 204—205° (decomp.). *Atropinebromoacetamide* forms bunches of matted needles, m. p. 204—205°; *atropineiodoacetamide* forms an indefinitely crystalline aggregate, m. p. 203—204° (decomp.).

E. F. A.

Caffeine. A. J. Ultée (*Chem. Weekblad*, 1910, 7, 32—34).—Additive products of caffeine with pyrogallol and phloroglucinol respectively have been prepared; they contain equimolecular proportions of their constituents. *Caffeine-pyrogallol*, $C_8H_{10}O_2N_4,C_6H_6O_3,4H_2O$, forms acicular crystals, m. p. 70°. The water of crystallisation is given off in a vacuum desiccator over sulphuric acid. The whole of the caffeine can be extracted by chloroform.

Caffeine-phloroglucinol, $C_8H_{10}O_2N_4,C_6H_6O_3,2H_2O$, forms ill-defined crystals, m. p. about 185°.

Theobromine is rapidly converted into caffeine by the action of methyl sulphate.

A. J. W.

Action of Grignard's Solutions on β-Cinchonine- and β-Quinine-ethiodides. Martin Freund and Fritz Mayer (*Ber*, 1909, 42, 4724—4728).—The β-ethiodide of cinchonine (Skraup and Norwall, Abstr., 1894, i, 391) has a constitution analogous to that of quinoline methiodide, and reacts with Grignard's reagent in much the same manner, yielding 1 : 2-diethyl-1 : 2-dihydrocinchonine and 2-phenyl-1-ethyl-1:2-dihydrocinchonine, $C_6H_4<\begin{matrix}\text{———}C(C_{10}H_{16}ON)\\ NEt\cdot CHEt(\text{or Ph})\end{matrix}>CH$. Quinine β-methiodide reacts in the same manner.

1 : 2-*Diethyl*-1 : 2-*dihydrocinchonine*, $C_{23}H_{32}ON_2$, crystallises from alcohol in needles, which sinter at 173° and are completely molten at 187°. Its salts do not crystallise, and the yield of the base is poor.

2-*Phenyl*-1-*ethyl*-1 : 2-*dihydrocinchonine*, $C_{27}H_{32}ON_2$, crystallises from dilute alcohol in slender needles, and has m. p. 135° after softening at 120°. The *hydriodide*, $C_{27}H_{32}ON_2,HI$, crystallises in plates, which decompose at 263°. The corresponding *hydrochloride* and *hydrobromide* have been prepared.

The *product* $C_{24}H_{34}O_2N_2$, obtained from quinine-β-ethiodide and ethyl magnesium bromide, could not be obtained in a crystalline form. The physiological properties of the products have been studied.

J. J. S.

Action of Chloroform on 2 : 5-Dimethylpyrrole. Giuseppe Plancher and U. Ponti (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 469—474).—The action of chloroform on 2 : 5-dimethylpyrrole in presence of alcoholic potassium hydroxide yields 2 : 5-dimethylpyrrole-3-aldehyde, 2-(or 3-)dichloromethyl-2 : 5-dimethylpyrrolenine, and 3-chloro-2 : 6-dimethylpyridine (compare Bocchi, Abstr., 1900, i, 357).

2 : 5-*Dimethylpyrrole*-3-*aldehyde*, $NH<\begin{matrix}CMe{:}C\cdot CHO\\ CMe{:}CH\end{matrix}$, forms colourless scales or mammillary crystals, m. p. 144°, and does not reduce Fehling's solution. Its *p-nitrophenylhydrazone*, $C_{13}H_{14}O_2N_4$ forms garnet-red crystals with metallic lustre, m. p. 234°. With

β-naphthylamine (1 mol.) and pyruvic acid (1 mol.) in alcoholic solution, the aldehyde (1 mol.) gives the corresponding *naphthacinchoninic acid*, m. p. 267°.

2 : 5-*Dimethyl*-(?)-*dichloromethylpyrrolenine*, $N<\begin{matrix}CMe\text{———}CH\\ \|\quad\quad\|\\ CMe(CHCl_2)\cdot CH\end{matrix}$ or $N<\begin{matrix}CMe{:}CH\\ |\quad\quad\\ CMe\cdot CH\cdot CHCl_2\end{matrix}$, is a heavy, colourless liquid having a basic odour resembling that of burnt almonds, and yields a *picrate*,

$$C_7H_9NCl_2,C_6H_3O_7N_3,$$

separating in pale yellow, rhombic scales, m. p. 144°. T. H. P.

Constitution of Hæmopyrrole and of Hæmopyrrolecarboxylic Acid. Oscar Piloty and E. Quitmann (*Ber.*, 1909, **42**, 4693—4703).—Pure hæmopyrrole can be obtained by carefully fractionating the crude product prepared by the method described previously (Abstr., 1909, i, 539). It has b. p. 114—115°/35 mm., m. p. 39°, and forms flat, quadratic plates. When fused, it forms a colourless oil with a pale fluorescence. The potassium derivative forms a colourless, crystalline powder, and the picrate has m. p. 108·5°. The constitution of hæmopyrrole has been settled by the action of nitrous acid. 2 : 4-Dimethylpyrrole (Knorr, Abstr., 1884, 1368), when treated with nitrous acid, yields the oxime of citraconimide, the 2-methyl group being eliminated. Pure hæmopyrrole and nitrous acid yield the oxime of methylethylmaleinimide, and as in this reaction a 2-methyl group is probably eliminated, hæmopyrrole should be a dimethylethylpyrrole :

$$NH<\begin{matrix}CMe{:}CMe\\ |\quad\quad\\ CH{=}CEt\end{matrix} \quad \text{or} \quad NH<\begin{matrix}CH{=}CMe\\ |\quad\quad\\ CMe{:}CEt\end{matrix}$$

2 : 5-Dimethylpyrrole (Paal, Abstr., 1885, 1206 ; Knorr, *ibid.*, 995) and nitrous acid yield the dioxime of dimethyltetraketone,

$$COMe\cdot C(:N\cdot OH)\cdot C(:N\cdot OH)\cdot COMe$$

(compare Thal, Abstr., 1892, 1074).

Methylethylmaleinimidemonoxime,

$$NH<\begin{matrix}C(:N\cdot OH)\cdot CMe\\ \|\quad\quad\|\\ CO\text{———}CEt\end{matrix} \quad \text{or} \quad NH<\begin{matrix}CO\text{———}CMe\\ \|\quad\quad\|\\ C(:N\cdot OH)\cdot CEt\end{matrix},$$

crystallises from water in colourless prisms, and has m. p. 201°. It is identical with the compound described previously (Abstr., 1909, i, 539) as melting at 206—207°. When hydrolysed with dilute sulphuric acid it yields methylethylmaleinimide.

Citraconimidemonoxime, $NH<\begin{matrix}CO\text{———}CMe\\ \|\quad\quad\|\\ C(:NOH)\cdot CH\end{matrix}$, forms small, colourless prisms, m. p. 223—224°, and when hydrolysed yields citraconic acid.

The oxime of hæmatic acid (*loc. cit.*, 540) when hydrolysed yields hæmatic acid.

It has not been found possible to decompose hæmopyrrole by means of hydroxylamine, although both 2 : 4- and 2 : 5-dimethylpyrroles are decomposed by this reagent (Ciamician and Zanetti, Abstr., 1890, 264, 1155).

A number of products are formed by reducing hæmatoporphyrin

with hydriodic acid and phosphorus; among these is an oil of low b. p., which yields a *picrate*, $C_{14}H_{18}O_7N_3$, m. p. 143—145°.

J. J. S.

New Cinchonic Acid Syntheses. Robert Schiff (*Ber.*, 1909, 42, 4918. Compare Borsche, Abstr., 1909, i, 955).—A claim for priority. R. V. S.

Quinoline Derivatives. Alfred Einhorn (*Ber.*, 1909, 42, 4854—4856).—[With Richard Feibelmann.]—*Ethyl quinoline-6-carboxylate hydrochloride* is prepared by boiling a suspension of the hydrochloride of *p*-quinolinecarboxylic acid in alcohol containing hydrogen chloride; it crystallises in bunches of needles, m. p. 210° (decomp.). The free acid forms matted needles, m. p. 50°.

The *hydrochloride* of *diethylaminoethyl quinoline-6-carboxylate*,

$$C_9H_6N\cdot CO\cdot O\cdot CH_2\cdot CH_2\cdot NEt_2,HCl,$$

prepared by the action of diethylaminoethanol on quinoline-6-carboxylic acid, is a faintly yellow-coloured, microcrystalline substance, m. p. 180°.

[With Maximilian Göttler.]—*Quinolineiodoacetamide*,

$$C_9NH_7I\cdot CH_2\cdot CO\cdot NH_2$$

crystallises from water in lustrous, orange-hued, refractive plates, or from alcohol in yellow needles, decomp. 250°; the solution has a green fluorescence. E. F. A.

Action of Magnesium *cyclo*Hexyl Bromide on Tetramethyldiaminobenzophenone. André Wahl and André Meyer (*Bull. Soc. chim.*, 1910, [iv], 7, 28—31. Compare Abstr., 1908, i, 890).—The authors have repeated the experiments of Schmidlin and Escher (Abstr., 1908, i, 163), and have succeeded in obtaining a small quantity of cyclo*hexylidenetetramethyldiaminodiphenylmethane*,

$$C_6H_{10}:C(C_6H_4\cdot NMe_2)_2,$$

m. p. 144—145°.

This was obtained by treating an ethereal solution of magnesium *cyclo*hexyl bromide with tetramethyldiaminobenzophenone and adding water. The precipitate, after the removal of magnesium compounds, consists mainly of unaltered ketone, from which the substance sought was separated by tedious fractionation from solutions in a mixture of acetone and ether, in which it is readily soluble. It crystallises in bright yellow prisms, and when dissolved in acetic acid gives with mild oxidising agents, such as lead peroxide, an intensely blue coloration, resembling that similarly obtained by Lemoult (Abstr., 1909, i, 836) with the *pp*-dialkyl derivatives of *as*-diphenylethylene. Since this new substance gives this reaction, it follows that the development of this blue dye is not due, as Lemoult supposed, to the specific influence of a characteristic hydrogen atom, since this is absent in the new substance. T. A. H.

Reaction of Nitrosoamides with Phenylhydrazine. Richard Willstätter and Arthur Stoll (*Ber.*, 1909, 42, 4872—4877).—When nitrosoformanilide reacts with phenylhydrazine (more than 2 mols.) in benzene at 0°, nitrogen is evolved and *s*-formylphenyl-

hydrazide is produced. This is not an instance of the migration of an acyl group, because nitrosoformo-*p*-toluidide and phenylhydrazine also yield *s*-formylphenylhydrazide, and nitrosoformanilide and *p*-tolylhydrazine yield *s*-formyl-*p*-tolylhydrazide. The reaction consists, therefore, in an acylation of the hydrazine by the nitrosoacylamide, which thus is converted into a diazo-compound; this, reacting with a second molecule of the hydrazine, forms a diazohydrazide, by the decomposition of which nitrogen and an aromatic hydrocarbon are produced:

(1) $CHO{\cdot}NPh{\cdot}NO + NHPh{\cdot}NH_2 = NHPh{\cdot}NH{\cdot}CHO + PhN_2{\cdot}OH$.

(2) $PhN_2{\cdot}OH + NHPh{\cdot}NH_2 = NH_2{\cdot}NPh{\cdot}N_2Ph + H_2O$.

(3) $NH_2{\cdot}NPh{\cdot}N_2Ph = 2C_6H_6 + 2N_2$.

The diazohydrazides can be isolated under suitable conditions. Nitrosoformanilide is very slowly introduced into a well-cooled dilute benzene solution of phenylhydrazine, the formylphenylhydrazine is removed, and the last portions are precipitated by the addition of light petroleum; the filtrate is evaporated, whereby a residue of diazobenzenephenylhydrazide, m. p. 71°, is obtained.

In a similar way, phenylhydrazine reacts with nitrosoacetanilide, nitrosophenylcarbamide, and nitrosomethylurethane, forming *s*-acetylphenylhydrazide, phenylsemicarbazide, and ethyl phenylcarbazinate respectively.

Other nitroso-compounds lose their nitroso-group by treatment with phenylhydrazine; nitrosophenylurethane, nitrosobenzanilide, diphenylnitrosoamine, and phenylethylnitrosoamine are converted into phenylurethane, benzanilide, diphenylamine, and phenylethylamine respectively; nitrous oxide is evolved in the last two cases.

Nitrosoformanilide and aniline in alcohol solution yield diazoaminobenzene and formanilide, the reaction following a course similar to the first-mentioned above. C. S.

New Phototropic Substances. II. Maurice Padoa and F. Graziani (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 559—564. Compare Abstr., 1909, i, 964).—The authors have obtained the following further results:

Cinnamaldehydephenylhydrazone, m. p. 171° (Fischer, Abstr., 1884, 1150, found 168°), is slightly phototropic.

Piperonaldehydephenylhydrazone, m. p. 106° (Rudolph, Abstr., 1889, 251, found 102—103°), is not phototropic.

p-Tolualdehydephenylhydrazone, $NHPh{\cdot}N{:}CH{\cdot}C_6H_4Me$, forms a yellow, crystalline powder, m. p. 121°, and is feebly phototropic.

With the *m*-tolylhydrazones, phototropy is observed, but less frequently and less intensely than with the *p*-tolylhydrazones; the corresponding ortho-compounds are not phototropic.

Benzaldehyde-m-*tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CHPh$, separates in slender, whitish-yellow needles, m. p. 100°, and exhibits phototropic properties.

Anisaldehyde-m-*tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CH{\cdot}C_6H_4{\cdot}OMe$, forms a yellow, crystalline powder, m. p. 111°, and is not phototropic.

Cuminaldehyde-m-*tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CH{\cdot}C_6H_4{\cdot}CHMe_2$, crystallises in yellowish-white needles, m. p. 136°, and is faintly phototropic.

Cinnamaldehyde-m-*tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CH{\cdot}CH{:}CHPh$, forms a yellow, crystalline powder, m. p. 131°, and is feebly phototropic.

Piperonaldehyde-m-*tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2$, forms canary-yellow needles, m. p. 131°, and is distinctly phototropic.

p-*Tolualdehyde*-m-*tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CH{\cdot}C_6H_4Me$, separates as an intensely yellow, crystalline powder, m. p. 121°, and is not phototropic.

Benzaldehyde-*o*-tolylhydrazone becomes coloured in the air even in the dark, but much more slowly than is the case with a phototropic compound (compare Reutt and Pawlewski, Abstr., 1904, i, 99). Such coloration appears to be favoured by moisture.

Anisaldehyde-o-*tolylhydrazone* crystallises in shining, white scales, m. p. 94°, and is not phototropic, but it softens in the air, giving ultimately a dark red syrup.

Cuminaldehyde-o-*tolylhydrazone* forms canary-yellow, shining scales, m. p. 91°, and is not phototropic; it readily changes in the air, its colour becoming red and its m. p. being lowered.

Piperonaldehyde-o-*tolylhydrazone* forms shining, yellow scales, m. p. 87°, and is not phototropic.

p-*Tolualdehyde*-o-*tolylhydrazone* crystallises in pale yellow scales, m. p. 109°, and is not phototropic; it readily becomes red in the air, especially in moist air. T. H. P.

Synthesis of Polypeptides. XXXII. Derivatives of *l*-Proline and of Phenylalanine. Emil Fischer and Andreas Luniak (*Ber.*, 1909, **42**, 4752—4759. Compare Fischer and Suzuki, Abstr., 1904, i, 771; Fischer and Reif, *ibid.*, 1908, i, 1007).—l-*Prolyl*-l-*phenylalanine*, $\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{-}NH\end{matrix}\!\!>\!CH{\cdot}CO{\cdot}NH{\cdot}CH\!<\!\begin{matrix}CO_2H\\ CH_2Ph\end{matrix}$, prepared by condensing *l*-prolyl chloride with *l*-phenylalanine ethyl ester and hydrolysing the resulting product with barium hydroxide, is identical with the dipeptide obtained by Osborne and Clapp (Abstr., 1908, i, 115) by the hydrolysis of gliadin with sulphuric acid.

The dipeptide is decomposed by pancreatin in a sodium carbonate solution at 36° during the course of forty-eight hours, and yields *l*-proline and *l*-phenylalanine.

l-*Prolyl*-d-*phenylalanine*, $C_{14}H_{18}O_3N_2,H_2O$, has also been prepared synthetically; it forms small, colourless prisms, has m. p. 223° (corr., decomp.), is more soluble in water than the isomeride, and has a bitter taste.

The *copper* salt, $C_{14}H_{16}O_3N_2Cu,2H_2O$, forms dark blue, microscopic prisms. J. J. S.

Aminopyrrolidone Derivatives from Mesityl Oxide and Aminolactones from Diacetone Alcohol. Moritz Kohn and Friedrich Bum (*Monatsh.*, 1909, **30**, 729—743. Compare Abstr., 1908, i, 819, 829).—A continuation of previous work. The 4-methylamino-1:2:2:4-dimethyl-5-pyrrolidone, $C_9H_{18}ON_2$, is now obtained as a colourless, crystalline mass, m. p. 32°, b. p. 121—122°/11 mm.

It reacts with ethylene oxide, forming a colourless, amorphous *compound*, $CMe_2<^{NMe\cdot CO}_{CH_2-CMe\cdot NMe\cdot CH_2\cdot CH_2\cdot OH}$; this yields a characteristic *aurichloride*, $C_{11}H_{22}O_2N_2,2HAuCl_4+H_2O$, decomp. 167°. The compound forms an additive *product* with methyl iodide, which was converted into the *methochloride* and analysed as the *platinichloride*, $C_{11}H_{22}O_2N_2,HCl,CH_3Cl,PtCl_4$, which crystallises in orange tablets.

4-*Ethylamino*-2 : 2 : 3-*trimethyl*-1-*ethyl*-5-*pyrrolidone*, $C_{11}H_{22}ON_2$, is a viscid oil, b. p. 127—131°/13—14 mm. The *compound* formed on interaction with ethylene oxide did not crystallise or yield crystalline salts, but was analysed in the form of the *platinichloride* of the *methochloride*, $C_{13}H_{26}O_2N_2,HCl,CH_3Cl,PtCl_4$.

4-Amino-5-keto-2 : 2 : 4-trimethyltetrahydrofuran forms a yellow *picrate*, m. p. 145—146°. The *picrate* of the corresponding 4-methylamino-compound crystallises in orange-yellow needles, m. p. 179°. The corresponding 4-dimethylamino-compound has b. p. 111°/11 mm., and yields a *picrate*, m. p. 175°, crystallising in well-formed citron-yellow needles.

4-*Ethylamino*-5-*keto*-2 : 2 : 4-*trimethyltetrahydrofuran*, synthesised from diacetone alcohol, ethylamine hydrochloride, and potassium cyanide, is a colourless, mobile liquid, b. p. 138—140°/15 mm. The *phenylcarbamide*, $C_{16}H_{22}O_2N_2S$, forms a colourless, sandy powder, m. p. 168°. The lactone further interacts with nitrous acid, forming a *nitroso*-derivative, $CMe_2<^{O-\!-CO}_{CH_2\cdot CMe\cdot N(NO)C_2H_5}$, which crystallises in colourless needles, m. p. 67°. E. F. A.

Action of Formaldehyde and Secondary Bases on Isatin. Alfred Einhorn and Maximilian Göttler (*Ber.*, 1909, 42, 4850—4852).—By the action of formaldehyde and secondary bases on isatin, two molecules of water are eliminated and condensation products formed, which are considered to be derived from the lactam formula: $CO<^{CO}_{C_6H_4}>N\cdot CH_2\cdot NRR'$.

ω-Diethylaminomethylisatin forms short, red crystals, aggregated in large clusters, m. p. 77—78°. *ω-Phenylethylaminomethylisatin* crystallises in deep red, reniform aggregates of thin plates, m. p. 98°.

E. F. A.

Synthesis of 5 : 7 : 5′ : 7′-Tetrabromoindigotin and 5 : 7 : 5′ : 7′-Tetrachloroindigotin. Negoïta Danaïla (*Compt. rend.*, 1909, 149, 1383—1385. Compare Abstr., 1908, i, 468, 798).—The constitution of the tetrahalogen derivatives of indigotin follows from the synthesis of these compounds by the reduction of 5 : 7-dibromoisatin chloride and 5 : 7-dichloroisatin chloride with hydrogen iodide (compare Grandmougin, this vol., i, 74).

Details of the absorption spectra of the compounds are given.

W. O. W.

Constitution of Indirubin. Louis C. Maillard (*Bull. Soc. chim.*, 1909, [iv], 5, 1153—1158).—In a previous paper (Abstr., 1902, i, 371) the author has shown that indigotin dissolved in chloroform to which hydrochloric acid has been added, slowly passes into indirubin, and on this ground has suggested (Abstr., 1903, i, 761) new formulæ for indigotin and indirubin, in which these are represented as polymerides, $C_{32}H_{20}O_4N_4$, of a supposed hemi-indigotin, $C_{16}H_{10}O_2N_2$. The evidence brought forward by Beckmann and Gabel (Abstr., 1906, i, 900) and Vaubel (*ibid.*, 989) that indigotin has the formula $C_{16}H_{10}O_2N_2$ is discounted by the fact that it was not obtained by physical determinations, but this objection does not apply to that derived from Wahl and Bagard's new synthesis of indirubin (Abstr., 1909, i, 300), which, in the opinion of these authors, supports the simple formula generally accepted for this substance. In this connexion the author points out that this acceptance implies (1) that mere standing of indigotin in acidified chloroform is sufficient to rotate the pyrrole nucleus from the α- to the β-position, or (2) that throughout the course of the new synthesis the oxindole nucleus does not remain unchanged in position.

T. A. H.

3-Hydroxyindazyl Derivatives. Paul Freundler (*Compt. rend.*, 1909, **149**, 1135—1137. Compare Abstr., 1906, i, 544; 1907, i, 158; 1909, i, 145).—*o*-Benzeneazobenzoic acid is obtained in 70—80% yield by condensing *o*-nitrosobenzoic acid with aniline. By treating this with phosphorus pentachloride and oxidising the product, a mixture of *o*-benzeneazochlorobenzoic acids is obtained, which, on treatment with phosphorus pentachloride, yields only 4 : 6-dichloro-3-hydroxyindazole, m. p. 187°. By treating *o*-benzeneazo-*p*-chlorobenzoic acid in the same way, *trichloro-3-hydroxyindazole*,

$$C_6H_2Cl\langle\begin{matrix}N\\|\\C(OH)\end{matrix}\rangle N\cdot C_6H_4Cl,$$

has been prepared; it forms needles, m. p. 209—210°.

The formation of a mixture of monochloro-derivatives when phosphorus pentachloride acts on *o*-carboxylic azo-compounds appears to indicate that the formation of chlorohydroxyindazoles is not due to direct chlorination. *Azoxybenzene-o-carboxylic acid*, prepared by condensing phenylhydroxylamine with *o*-nitrosobenzoic acid, crystallises in yellow prisms, m. p. 118°.

Hubner's 3 : 5-dibromoanthranilic acid does not condense with nitrobenzene. The *acetyl* derivative of the acid has m. p. 221° (decomp.); the *methyl* ester forms spangles, m. p. 91°. W. O. W.

Pyrimidines. XLIX. Thio-derivatives of Thymine and the Preparation of Thymine. Henry L. Wheeler and David F. McFarland [and, in part, Walter F. Storey] (*Amer. Chem. J.*, 1910, **43**, 19—36).—Wheeler and Liddle (Abstr., 1909, i, 60) have shown that in the preparation of uracil a larger yield is obtained by condensing ethyl sodioformylacetate with thiocarbamide than by condensing it with ψ-ethylthiocarbamide. Experiments have therefore been carried out in order to ascertain whether the preparation of thymine could be improved in a similar manner. It has been found that when ethyl

sodioformylpropionate is condensed with thiocarbamide in aqueous solution, the yield of 2-thiothymine is only about one-half of that obtained by the use of ψ-ethylthiocarbamide, but that if the reaction is carried out in alcoholic solution, a much larger yield is obtained, amounting to about 22·6% of the calculated quantity, and nearly identical with that furnished by the ψ-ethylthiocarbamide condensation.

2-*Thiothymine*, $NH<^{CS-NH}_{CO\cdot CMe}>CH$, forms fairly stout prisms, is soluble in water at 20° to the extent of 0·133%, and is readily converted into thymine by heating its aqueous solution with chloroacetic acid. Thymine is soluble in water at 23° to the extent of 0·303%. 2-Thiothymine has a more pronounced acid character than thymine; its *sodium*, *potassium*, and *copper* salts are described.

2-*Benzylthiol*-5-*methyl*-6-*pyrimidone*, $NH<^{C(S\cdot CH_2Ph):N}_{CO-----CMe}>CH$, m. p. 204—205°, obtained by the action of benzyl chloride on the potassium salt of 2-thiothymine, forms colourless needles.

6-*Thio*-2-*ethylthiol*-5-*methylpyrimidine*, $NH<^{C(SEt):N}_{CS-CMe}>CH$, m. p. 181°, obtained by warming 6-chloro-2-ethylthiol-5-methylpyrimidine (Wheeler and Johnson, Abstr., 1904, i, 624) with a solution of potassium hydrogen sulphide, crystallises in prismatic needles, and, when heated at 215° in a current of hydrogen chloride, is converted into 2 : 6-*dithiothymine*, $NH<^{CS\cdot NH}_{CS\cdot CMe}>CH$, m. p. 281° (decomp.), which forms small, bright yellow needles.

When 6-thio-2-ethylthiol-5-methylpyrimidine is boiled with concentrated hydrochloric acid for one and a-half hours, it is converted into thymine, but, on less vigorous treatment, 6-*thiothymine*,

$$NH<^{CO\cdot NH}_{CS\cdot CMe}>CH,$$

m. p. 330° (decomp.), is produced, which forms bright yellow, silky needles. By the action of methyl iodide on 6-thiothymine in presence of potassium hydroxide, 6-*methylthiol*-5-*methyl*-2-*pyrimidone*,

$$N<^{CO-----NH}_{C(SMe)\cdot CMe}>CH,$$

m. p. 205—211°, is obtained, which forms pale yellow, prismatic needles. When this substance is heated with methyl iodide in presence of potassium hydroxide, 6-*methylthiol*-3 : 5-*dimethyl*-2-*pyrimidone*,

$$N<^{CO-----NMe}_{C(SMe)\cdot CMe}>CH,$$

m. p. 83°, is obtained, which forms white, prismatic needles, and, when boiled with concentrated hydrochloric acid, is converted into 3-methylthymine (Johnson and Clapp, Abstr., 1908, i, 835). E. G.

Derivatives of Piperazine. Antoine P. N. Franchimont and E. Kramer (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 452—454). —Van Dorp (Abstr., 1909, i, 327), who prepared piperazinediacetic acid together with the corresponding diamide and dinitrile, failed to esterify the acid; this has now been effected. The acid forms a compound with sulphuric acid, and when this is heated with excess of

this acid and alcohol, the crystalline compound of sulphuric acid with the ester is obtained. The ester is freed by treatment with bases under a layer of ether or benzene. The *methyl* ester is a colourless substance, m. p. 63°; the *ethyl* ester, m. p. 47·5°, is also crystalline. Being tertiary amines, both not only combine with acids, but also with methyl iodide, but of this they only unite with one molecule. The compound obtained in this way from the methyl ester has m. p. 144—145°, that from the ethyl ester, m. p. 143°. The compound *piperazinediethylenediamine*,

$$NH_2\cdot CH_2\cdot CH_2\cdot N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CH_2\cdot NH_2,$$

was obtained by reduction of the dinitrile by means of sodium and alcohol. The anhydrous compound, m. p. 40—41°, is hygroscopic, yields with water a crystalline compound, m. p. 63°, and with 4HCl a non-hygroscopic, crystalline *hydrochloride*. The *picrate* and *oxalate* form yellow and colourless crystals respectively; the *picryl* derivative is crystalline and decomposes at 238°, and a *benzoyl* derivative was obtained. Similar derivatives of the lower homologue of the above, namely, *piperazinedimethylenediamine*, were prepared. This compound could not be obtained from the acetamide by Hoffmann's method, so that it was necessary to resort to the sodium and alcohol reduction of *piperazinediformonitrile*. This substance, prepared from bromocyanogen and piperazine in aqueous solution with addition of alkali, crystallises in leaflets, m. p. 168°, and combines neither with methyl iodide, benzene, nor oxalic acid. G. S. W.

Ketochlorides and Quinones of Heterocyclic Compounds and Their Transformation Products. III. Ketochlorides and Quinones of Phenyl-ψ-aziminobenzene [2 : 1 : 3-Benztriazole]. Theodor Zincke and E. Scharff (*Annalen*, 1909, **370**, 297—314).—A preliminary note of this investigation has appeared already (compare Zincke and Petermann, Abstr., 1899, i, 135). A complete parallelism is shown to exist between phenyl-ψ-aziminobenzene [2 : 1 : 3-benztriazole] and phenylaziminobenzene [1 : 2 : 3-benztriazole], the different structure of the nitrogen ring having no marked influence on the chemical properties (compare Zincke, Stoffel, and Petermann, Abstr., 1900, i, 524; Zincke and Petermann, Abstr., 1901, i, 104).

5-Amino-2-phenyl-2 : 1 : 3-benztriazole has m. p. 183° (compare Kehrmann and Messinger, Abstr., 1892, 889); the *sulphate* and *hydrochloride* crystallise in colourless needles; the *acetyl* derivative, $C_{14}H_{12}ON_4$, crystallises in faintly pink, silky, slender needles, m. p. 192°.

6-Chloro-5-nitro-2-phenyl-2 : 1 : 3-benztriazole, $NPh<\begin{matrix}N\cdot C:CH\cdot C\cdot NO_2\\ |\quad\quad |\quad\quad ||\\ N\cdot C:CH\cdot CCl\end{matrix}$, is prepared by boiling a solution of 1 : 3-dichloro-4 : 6-dinitrobenzene in 96% alcohol with phenylhydrazine and crystalline sodium acetate; it forms pale yellow needles, m. p. 196°, and when reduced with hydrochloric acid and tin yields the corresponding *amino*-compound, $C_{12}H_9N_4Cl$, small, glistening, brownish-yellow leaflets and needles,

m. p. 221—222°, the *acetyl* derivative of which crystallises in slender, white needles, m. p. 221°.

4 : 5 : 5 : 7 : 7-*Pentachloro*-6-*keto*-2-*phenyltetrahydro*-2 : 1 : 3-*benztriazole*, $NPh<^{N\cdot C-CCl_2-CO}_{N\cdot C\cdot CHCl\cdot CCl_2}$, is formed together with small quantities of the corresponding *hexachloroketochloride* by the action of chlorine on the stannichloride of either of the amino-compounds just described; it forms stout, yellowish-green, monoclinic crystals, m. p. 128°, and when reduced yields a mixture of the corresponding *dichlorohydroxy*- and *trichlorohydroxy*-compounds, which could not be resolved. 4 : 5 : 7 : 7-*Tetrachloro*-6-*keto*-2-*phenyl*-6 : 7-*dihydro*-2 : 1 : 3-*benztriazole*, $C_{12}H_5ON_4Cl_4$, prepared by boiling the pentachloro-compound just described with a solution of potassium acetate in acetic acid, crystallises in slender, yellow needles, m. p. 168°, and when reduced with stannous chloride yields 4 : 5 : 7-*trichloro*-6-*hydroxy*-2-*phenyl*-2 : 1 : 3-*benztetrazole*,

$$C_{12}H_6ON_3Cl_3,$$

slender, white needles, m. p. 167—168°, the *acetyl* derivative of which, $C_{14}H_8O_2N_3Cl_3$, crystallises in glistening, white needles, m. p. 179—180°. The trichlorophenol is oxidised by nitric acid (D 1·4) in glacial acetic acid, yielding 4 : 5-*dichloro*-6 : 7-*diketo*-2-*phenyl*-6 : 7-*dihydro*-2 : 1 : 3-*benztetrazole*, $NPh<^{N\cdot C-CO-CO}_{N\cdot C\cdot CCl:CCl}$, large, red crystals, m. p. 191°. The latter substance undergoes the following changes: (1) When reduced with stannous chloride, it yields 4 : 5-*dichloro*-6 : 7-*dihydroxy*-2-*phenyl*-2 : 1 : 3-*benztriazole*, $C_{12}H_7O_2N_3Cl_2$, which crystallises in slender, white needles, sinters at about 130°, m. p. 154—155° (decomp.) when heated slowly, m. p. 170° (decomp.) when heated rapidly; the *diacetate*, $C_{16}H_{11}O_4N_3Cl_2$, forms glistening, slender, white needles, m. p. 189—190°. (2) It is converted by a hot 20% aqueous solution of sodium carbonate into 5-*chloro*-6-*hydroxy*-4 : 7-*diketo*-2-*phenyl*-4 : 7-*dihydro*-2 : 1 : 3-*benztriazole*, $C_{12}H_6O_3N_3Cl$, large, brownish-yellow crystals, m. p. 265—266°, which, when boiled with nitric acid (D 1·4), yields the corresponding *tetraketo*-derivative, $NPh<^{N\cdot C\cdot CO\cdot CO}_{N\cdot C\cdot CO\cdot CO}$, crystallising in almost colourless needles, m. p. 165—170° (decomp.). (3) When treated with aniline in glacial acetic acid it yields 5-*chloro*-6-*hydroxy*-7-*keto*-4-*phenylimino*-2-*phenyl*-4 : 7-*dihydro*-2 : 1 : 3-*benztriazole*,

$$C_{18}H_{11}O_2N_4Cl,$$

which crystallises in slender, brownish-red needles with a bronzy reflex, sinters at 228°, m. p. 234—236° (decomp.).

Pentachloroketo-2-phenyltetrahydro-2 : 1 : 3-benztriazole, when acted on by a cold 5% aqueous solution of sodium hydroxide, yields the *acid*, $NPh<^{N\cdot C\cdot CCl_2\cdot CO_2H}_{N\cdot C\cdot CCl:CHCl}$, which crystallises in slender, white needles, m. p. 62—63°; the *methyl* ester, $C_{13}H_9O_2N_3Cl_4$, forms slender, silky, white needles, m. p. 67—68°. An aqueous solution of the sodium salt of the acid when boiled yields the *acid*, $N_3Ph<^{C\cdot CO\cdot CO_2H}_{C\cdot CCl:CHCl}$, long, white needles, m. p. 177°, the *methyl* ester of which, $C_{13}H_9O_3N_3Cl_2$,

crystallises in glistening, white needles, m. p. 152—153°; the acid just described also results from the action of a 5% aqueous solution of sodium hydroxide on dichlorodiketophenyldihydro-2 : 1 : 3-benztriazole.

W. H. G.

Isomeric Thiourazoles. Max Busch, J. Reinhardt, and O. Limpach (*Ber.*, 1909, 42, 4763—4769. Compare Marckwald and Sedlaczek, Abstr., 1896, i, 231; Busch, *ibid.*, 1902, i, 322; Busch and Opfermann, *ibid.*, 1904, i, 630).—It is shown that the triazoles obtained from α-diarylthiosemicarbazides (Marckwald, Abstr., 1899, i, 503) also exist in two isomeric forms: a labile form, for example, 1 : 4-diphenyl-5-thiourazole, $SC<^{NPh\cdot NH}_{NPh\cdot CO}$, and a stable form:

$$\begin{matrix} N{=}{=}C{-}{-}{-}{-} \\ |\ O< \\ PhN{-}{-}C(SH) \end{matrix}\!\!>NPh$$ (compare Marckwald).

A mixture of the two compounds is formed when finely-divided α-diphenylthiosemicarbazide is suspended in benzene and shaken for two to three hours with an excess of a toluene solution of carbonyl chloride. The two urazoles are removed by shaking with 5% sodium hydroxide solution. The labile compound is precipitated on the addition of acetic acid to the alkaline liquid, and the stable compound on the addition of hydrochloric acid to the filtrate. If the mixture is shaken for a longer time, the amount of stable compound tends to increase at the expense of its isomeride. The benzene solution contains unaltered thiosemicarbazide and phenylanilinothiobiazolone (Freund and Kuh, Abstr., 1890, 1440). The labile compound crystallises in colourless needles, melts at 139—140°, but is immediately transformed into the stable compound, m. p. 220°. Its *sodium* derivative crystallises in slender, felted needles, m. p. 60°, and reacts with methyl iodide at 100°, yielding diphenylmethylurazole (Busch and Heinrichs, Abstr., 1901, i, 617). The *silver* salt is insoluble, and with methyl iodide yields the O-*methyl* derivative, $SC<^{NPh\cdot N}_{NPh\cdot C\cdot OMe}$, m. p. 88°. When benzoylated in pyridine solution the thiourazole yields N-*benzoyldiphenylthiourazole*, $C_{21}H_{15}O_2N_3S$, as yellow needles, m. p. 146°, which are stable in the presence of alkalis.

The 5-thiol-1 : 4-diphenyl*endo*-oxydihydrotriazole, when oxidised with ferric chloride, yields a *disulphide*, $(C_{14}H_{10}ON_3S)_2$, in the form of orange-yellow needles, m. p. 231—232°. The thiol yields the 5-*benzoyl* derivative,

$$\begin{matrix} N{:}C{-}{-}{-}{-}{-} \\ |\ >O \\ PhN{\cdot}C(S{\cdot}COPh) \end{matrix}\!\!>NPh$$, as colourless needles, m. p. 189°. The *sodium* derivative of the thiol has m. p. 121°, and with methyl iodide and methyl alcohol at the ordinary temperature yields methyl mercaptan and 1 : 4-diphenyl-2-methylurazole.

The following diarylthiosemicarbazides also yield pairs of isomeric thiourazoles with the m. p. indicated:

2 : 4-Diarylthiosemicarbazide.	Thiourazole.	Thiol*cudo*-oxydihydrotriazole.
4-Phenyl-2-*m*-tolyl	125°	259°
4-Phenyl-2-*m*-bromophenyl	118—119°	257
4-Phenyl-2-*m*-chlorophenyl	108—110	259—260
4-Phenyl-2-*β*-naphthyl	133—134	295
4-Phenyl-2-*p*-tolyl	144	239—240
4-Phenyl-2-*p*-bromophenyl	169—170	255

J. J. S.

Organic Salts of Violuric Acid. Th. Zerewitinoff (*Ber.*, 1909, 42, 4802—4808).—Violuric acid forms intensely coloured salts with primary, secondary, and tertiary aliphatic amines and diamines, also with pyridine, piperidine, alkaloids, and some aromatic amines. The salts with primary aliphatic amines exist in two main forms, coloured blue and red (compare Hantzsch, Abstr., 1909, i, 331), but usually mixtures of these are obtained resulting in violet or blue, or reddish-violet salts. Usually only one form is stable, the conversion of one into the other readily taking place in the presence of moisture. Thus *n*-propylamine, *n*-butylamine, and *n*-amylamine violurates are obtained as violet salts from alcoholic solution, but become blue on exposure to moist air, and remain blue when dried in a desiccator.

Salts of violuric acid with normal primary amines are usually red or violet in colour; those derived from primary *iso*-compounds are more often blue. The blue modification is the one generally obtained from aqueous solution.

The amine violurates are prepared by mixing the components in equimolecular proportions in alcoholic solution. The salt readily separates, and may be crystallised from alcohol or water.

Methylamine violurate is obtained violet from alcoholic solution, or blue when methyl ethyl ketone is the solvent, the violet being the stable form. *Ethylamine violurate* is at first obtained blue, but rapidly passes into the stable red form. n-*Propylamine violurate* is at first obtained blue in alcoholic solution, but the salt turns reddish-violet when left in contact with the solvent. The violet form retains its colour when dried, but changes to blue again in presence of moisture. iso*Propylamine violurate* is blue; n-*butylamine violurate* is violet, changing to blue on exposure. iso*Butylamine violurate* forms violet-blue plates or blue needles. n-*Amylamine violurate* is likewise violet, changing to blue. iso*Amylamine violurate* is at first blue, but becomes violet on recrystallisation. tert.-*Amylamine violurate* is also blue; similarly, iso*hexylamine violurate*, but this is violet when crystallised from water. *Heptylamine violurate* is similar.

Diamine salts having the formula

$$R\cdot NH_3\cdot O\cdot C\begin{matrix}N{-}{-}CO\\ NH\cdot CO\end{matrix}C{:}N\cdot O\cdot NH_3\cdot R$$

are prepared by keeping the monoamine violurate in presence of the corresponding amine in a desiccator.

*Di*iso*butylamine violurate* and *di*-n-*amylamine violurate* are both reddish-violet in colour.

The amine violurates dissolve in pyridine with a blue coloration. The active hydrogen atoms were determined at normal temperature

and at 85° by means of magnesium methyl iodide by the method previously described (Abstr., 1908, i, 598). The results indicate that at normal temperature only two hydrogen atoms of the NH_3 radicle are active, but at 85° all three react. E. F. A.

Hæmopyrrole. II. *Z.* Leyko and Leon Marchlewski (*Biochem. Zeitsch.*, 1909, 22, 464—470; *Bull. Acad. Sci. Cracow*, 1909, 583—588. Compare Abstr., 1908, i, 710).—Altogether four products have been obtained by the action of benzenediazonium salts on hæmopyrrole. The main product has the formula

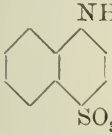
$$C_8H_{11}N(N_2Ph)_2,HCl.$$

The authors now describe a method for preparing the second product, $N_2Ph{\cdot}C_8H_{11}N{\cdot}C_8H_{11}N{\cdot}N_2Ph,HCl$, which melts at 268°. It can be separated from the chief product by means of chloroform, in which it is much more soluble, forming a bluish-violet solution, from which it can be precipitated by alcohol.

By means of sodium acetate the free base of this dye can be obtained. The authors give the measurements of the absorption bands of the chlorine-containing substance in chloroform solution. The results obtained are regarded as of importance as showing that hæmopyrrole corresponds with the formula $C_8H_{13}N$, and not $C_7H_{11}N$, and also that it is admixed with a second product corresponding with the formula $C_8H_{12}N{\cdot}C_8H_{12}N$, the representative of a new class of pyrrole derivatives. S. B. S.

Action of Sulphites on Aromatic Amino- and Hydroxyl Compounds. VIII. Behaviour of Hydrazines, especially of Phenylhydrazine, in the Sulphite Reaction. Hans Th. Bucherer and Ernst F. Sonnenburg (*J. pr. Chem.*, 1910, [ii], 81, 1—48. Compare Abstr., 1909, i, 787).—A difference has been observed in the behaviour of naphthalene derivatives of the α- and the β-series containing only one auxochromic group when these compounds undergo prolonged boiling with phenylhydrazine and 36% sodium hydrogen sulphite. The reactions are complicated by the interaction of the two last-mentioned substances to form sodium phenylhydrazinesulphonate, from which the desired reaction product cannot be separated. After decomposing the latter, however, by alkalis and by acids, the nature of the secondary products throws some light on the constitution of the primary products in the sulphite reaction. Thus amines and naphthols of the α-series (except α-naphthol itself and 1-naphthylamine-5-sulphonic acid) yield *s*-hydrazinesulphonates, $NHR{\cdot}NPh{\cdot}SO_3Na$ or $NHPh{\cdot}NR{\cdot}SO_3Na$, which are converted by alkali into benzeneazonaphthalene derivatives, and by acid into nuclear sulphonic acids of the carbazoles, and also to some extent into diamino-compounds by the benzidine transformation. Amines and naphthols of the β-series and also the two above-mentioned exceptions of the α-series yield, after treatment with phenylhydrazine and sodium hydrogen sulphite, carbazole-*N*-sulphonic acids, which are probably produced from an initially-formed hydrazo-compound by intramolecular indole condensation; the absence of any hydrazo-compound among the primary products of the reaction is proved by the non-production of azo-compounds by treatment with alkali (compare Abstr., 1908, i, 455).

The reaction typical of members of the α-series is best exemplified by 1-naphthol-4-sulphonic acid, the only instance in which the initial hydrazo-compound can be separated from the sodium phenylhydrazine-sulphonate formed simultaneously. 1-Naphthol-4-sulphonic acid is boiled with phenylhydrazine and 36% sodium hydrogen sulphite for seven and a-half hours, and the white, crystalline product is extracted with boiling 95% alcohol. The alcoholic extract deposits on cooling colourless crystals, which are freed from sodium phenylhydrazine-sulphonate by treatment with benzene and with alcohol; the purified product has the composition



$C_{16}H_{12}O_6N_2S_2Na_2$,

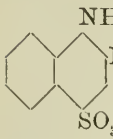
and is the *hydrazo*-compound, probably having the annexed constitution. By treatment with sodium hydroxide, it yields benzeneazo-α-naphthalene and benzeneazo-α-naphthalenesulphonic acid (each of which can be reduced to diamino-compounds), and by heating with hydrochloric acid (3 : 1) it is converted into α-phenonaphthacarbazole and a diamino-compound. 1-Naphthylamine-4-sulphonic acid behaves in the same way, and yields the same products, and so also does 1-naphthylamine-6-sulphonic acid, the reaction product being converted by dilute sodium hydroxide on the water-bath into benzeneazo-α-naphthalene-6-sulphonic acid, and by strong hydrochloric acid into *α-phenonaphthacarbazole-6-sulphonic acid*, $SO_3H\cdot C_{10}H_5<\overset{NH}{\underset{C_6H_4}{|}}$, and a diamino-compound.

By prolonged heating with phenylhydrazine and 36% sodium hydrogen sulphite, α-naphthol yields pheno-α-naphthazole-*N*-sulphonic acid, which cannot be isolated in a solid state, but yields phenonaphthacarbazole when heated with concentrated hydrochloric acid. In a similar way, the product from 1-naphthylamine-5-sulphonic acid yields α-phenonaphthacarbazole-5-sulphonic acid (probably obtained from the *N*/5-disulphonic acid); that from 2-naphthol-1-sulphonic acid or 2 naphthylamine-1-sulphonic acid yields 2 : 1-phenonaphthacarbazole in small amount and 2 : 3-phenonaphthacarbazole-1-sulphonic acid; that from 2-naphthol-6-sulphonic acid yields phenonaphthacarbazole-6-sulphonic acid, and that from 2-naphthol-3 : 6-disulphonic acid yields a carbazole-3 : 6-disulphonic acid.

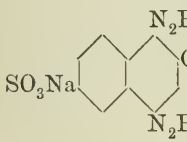
The action of phenylhydrazine and sodium hydrogen sulphite on naphthalene derivatives containing two auxochromic groups is somewhat different from that on derivatives containing only one. Carbazoles are not formed. Thus 1-amino-2-naphthol-4-sulphonic acid yields a yellow *solid* and a yellow solution. The solid has the composition $C_{22}H_{19}O_3N_4SNa$, and by treatment with hot sodium hydroxide yields a bluish-red *dye*, from which hydrochloric acid eliminates phenylhydrazine. The yellow solution by treatment with warm concentrated sodium hydroxide yields sodium 1-benzeneazo-2-naphthol-4-sulphonate, 2-benzeneazo-1-naphthol-4-sulphonate, and 2-benzeneazo-1-naphthol. Bearing in mind that the sulphite reaction proceeds thus :

$$R\cdot NH_2 \text{ or } R\cdot OH \xrightarrow{NaHSO_3} R\cdot O\cdot SO_2Na \xrightarrow{PhN_2H_3} R\cdot NH\cdot NHPh,$$

there appears to be little doubt that the yellow solid has the annexed constitution, and that it yields the preceding azo-compounds by loss of phenylhydrazine from position 1 or 2 and simultaneous oxidation when treated with alkali. Similarly, 1-amino-2-naphthol-3 : 6-disulphonic acid also yields two yellow products, the one soluble, the other insoluble, which are converted by alkali into red azo dyes.

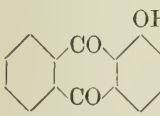


The action of phenylhydrazine and sodium hydrogen sulphite on certain azo-dyes follows a similar course. By heating 1-benzeneazo-2-naphthol-3 : 6-disulphonic acid with phenylhydrazine (or hydrazine hydrate) and sodium hydrogen sulphite, a yellow solid and a yellow solution are obtained, from each of which the original dye is recovered by alkali. The reaction in the case of 1-benzeneazo-2-naphthol-6-sulphonic acid is more profound. Again, a yellow *solid* and a yellow solution are obtained. The latter regenerates the original dye by treatment with alkali, and probably contains the hydrogen sulphite compound of the dye. The yellow solid, the analysis of which accords with the constitution $SO_3Na\cdot C_{10}H_4(NH\cdot NHPh)_2(NH\cdot NPh\cdot SO_3Na)$, is stable towards cold alkali, but is converted by warm dilute sodium hydroxide into a bluish-red *dye*, the analysis of which points to the annexed constitution.



The behaviour of a mixture of 1-benzeneazo- and 1-toluneazo-2-naphthol-6-sulphonic acid, or of 1-xyleneazo-2-naphthol-3 : 6-disulphonic acid, with phenylhydrazine and sodium hydrogen sulphite is very similar to the preceding.

The behaviour of alizarin-red-*S* with phenylhydrazine and sodium hydrogen sulphite has also been examined. The product is a yellowish-brown *substance*, which resembles the original dye in several respects but differs from it in the colour of its alkaline solution and in producing a more violet shade on chromed wool. It has probably the annexed constitution, and regenerates alizarin-red-*S* and phenylhydrazine when heated with dilute hydrochloric acid.

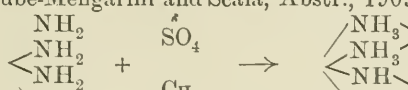


No condensation takes place when 1-naphthylamine- or 1-naphthol-4-sulphonic acid is heated with sodium hydrogen sulphite and hydrazobenzene, either together or successively ; the product contains azobenzene, benzidine, and its *N*-sulphonic acid. The latter is obtained almost quantitatively when azobenzene, ammonium hydrogen sulphite, and ammonium hydroxide (D 0·88) are heated for twenty-four hours at 100—110° under 2 atmospheres pressure. C. S.

Compounds of Copper with Egg-Albumin. Alberto Scala and Giuseppe Bonamartini (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 551—559).—Further examination of the acid copper albumin obtained from copper sulphate and egg-albumin (compare Bonamartini and Lombardi, Abstr., 1909, i, 72) shows that, after washing, this compound does not contain copper and sulphuric acid in the proportions in which they exist in copper sulphate, the copper always being

in excess. In fact, making allowance for the sulphuric acid yielded on analysis by the sulphur of the albumin, it would appear that the whole of the sulphuric acid is eliminated by washing, together with the larger part of the copper.

These observations may be explained by assuming that the copper sulphate combines with lateral amino-groups of the albumin molecule (compare Traube-Mengarini and Scala, Abstr., 1909, ii, 603) thus :



giving a compound in which the degrees of dissociation and hydrolysis of the group $\begin{matrix}NH_3\\NH_3\end{matrix}\!>\!SO_4$ are greater than those of the group $\begin{matrix}NH\\NH\end{matrix}\!>\!Cu$, so that whilst the one group tends to become completely removed, the other (Cu) tends towards a limit. If, then, compounds containing at first different proportions of copper are washed, they should yield compounds of constant type, and this is found approximately to be the case.

That this explanation is the true one is shown by the observation that, when an egg-albumin solution is treated with copper sulphate in slight excess and then with sodium hydroxide solution, a compound is obtained with a proportion of copper greater than is ever observed when no sodium hydroxide is employed; the alkali tends to detach the SO_4 groups, and at the same time introduce more Cu groups into the molecule. T. H. P.

The Scission Products of the Nucleo-protein of Milk Glands. John A. Mandel (*Biochem. Zeitsch.*, 1909, 23, 245—249).—The amino-acids and hexone bases obtained by the hydrolysis of the nucleo-protein were estimated and compared with the hydrolysis products of caseinogen. There is a decided similarity in the numbers obtained, which indicate that caseinogen is possibly a degradation product of the nucleo-protein of milk glands, and produced from the latter by a scission of carbohydrates, purine, and pyrimidine bases. Hammarsten's method was employed in the preparation of the nucleo-protein. S. B. S.

Studies on Enzymes. II. Measurement and Meaning of the Concentration of the Hydrogen Ions in Enzymatic Processes. Sören P. L. Sörensen (*Biochem. Zeitsch.*, 1909, 22, 352—356; *Compt. rend. Lab. Carlsberg*, 1909, 8, 1—168. Compare Abstr., 1909, i, 861). —It was found that the secondary sodium phosphate employed for preparing the 1/15 mol. standard solution contained 3—4% of the primary salt. New determinations with a pure salt were accordingly made, and the results are given in a table. The new values, p_H, do not, however, differ essentially from the ones previously given except in the mixtures having the greatest alkalinity. In neutral or nearly neutral mixtures, the difference is quite small, and is sometimes positive and sometimes negative, so that the old values are retained for the whole curve. N. H. J. M.

[The Enzymes of Gum-acacia and certain other Gums.] Viktor Grafe (*Zeitsch. physiol. Chem.*, 1909, **63**, 106—108).—A reply to some criticisms of Reinitzer (Abstr., 1909, i, 751). S. B. S.

Preparation of Hydroxyarylarsenious Oxides. Farbwerke vorm. Meister Lucius & Brüning (D.R.-P. 213594).—The action of mild reducing agents, such as hydrogen iodide, sulphurous acid, phenylhydrazine, phosphorus trichloride, or thionyl chloride on hydroxyphenylarsinic acids leads to the formation of hydroxyarsenious oxides.

p-*Hydroxyphenylarsenious oxide*, $OH\cdot C_6H_4\cdot AsO$, a colourless, crystalline powder, readily soluble in water or alcohol, is prepared by reducing sodium *p*-hydroxyphenylarsinate with potassium iodide and dilute sulphuric acid.

p-*Arsenophenol*, $OH\cdot C_6H_4\cdot As{:}As\cdot C_6H_4\cdot OH$, is precipitated in yellow flakes when the foregoing compound is warmed in neutral solution with sodium hypochlorite. F. M. G. M.

o-Aminoarylarsinic Acids. Ludwig Benda (*Ber.*, 1909, **42**, 3619—3622. Compare Ehrlich and Bertheim, Abstr., 1907, i, 812; O. and R. Adler, 1908, i, 492; Benda and Kahn, 1908, i, 591; Bertheim, 1908, i, 590).—Arylamines with a substituent in the para-position with respect to the amino-group condense with arsenic acid, yielding *o*-aminoarylarsinic acids, but the yields are not good. These ortho-arsanilic acids closely resemble the corresponding para-compounds in most of their properties, and can be readily acylated and diazotised. 4-*Aminotolyl-5-arsinic acid*, $NH_2\cdot C_6H_3Me\cdot AsO(OH)_2$, obtained from *p*-toluidine and arsenic acid at 195—200°, crystallises from dilute alcohol in felted needles, m. p. 176°. *m*-Xylidine and arsenic acid yield 4-*amino*-m-*xylene-5-arsinic acid*, $NH_2\cdot C_6H_2Me_2\cdot AsO(OH)_2$, m. p. 199—200°, and *p*-chloroaniline and arsenic acid, 4-*chloro*-1 : 2-*arsanilic acid*. $NH_2\cdot C_6H_3Cl\cdot AsO(OH)_2$, m. p. 207°. The position of the arsinic acid radicle can be determined by replacement by iodine. J. J. S.

Preparation of Carbamide and of Thiocarbamide Derivatives of *p*-Aminophenylarsinic Acids. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 213155).—The action of cyanic or thiocyanic acids (or the corresponding esters) on *p*-aminophenylarsinic acid or its derivatives yields crystalline compounds having the general formula $NRR_1\cdot CR_2\cdot NH\cdot C_6H_4\cdot AsO(OH)_2$, where R and R_1 may be either hydrogen, aryl, or alkyl groups, and R_2 either sulphur or oxygen; these compounds are sparingly soluble in cold water or dilute mineral acids, and therapeutically less toxic than the acyl *p*-aminophenylarsinic acids. The following examples are mentioned: *carbamidoarsanilic acid*, *thiocarbamidoarsanilic acid*, *phenylcarbamidoarsanilic acid*, *methylcarbamidoarsanilic acid*, *carbamido-o-methylarsanilic acid*, and *carbamidoanthranilic-arsinic acid*. F. M. G. M.

Organic Chemistry.

Oxidation of Unsaturated Compounds by means of Organic Peroxides. Eduard Lippmann (*Ber.*, 1910, **43**, 464. Compare Prileschaéeff, this vol., i, 86).—The addition of benzoyl peroxide to amylene, and the subsequent hydrolysis to *iso*diamylene oxide, was studied by the author in 1884 (Abstr., 1885, 366).

J. J. S.

Condensation of *sec.*-Butyl Alcohol with its Sodium Derivative. Marcel Guerbet (*Compt. rend.*, 1910, **150**, 183—185. Compare Abstr., 1902, i, 130, 583, 657; 1908, i, 162, 635).—When *sec.*-butyl alcohol is heated with its sodium derivative at 200—220° there is formed a mixture of two alcohols: (1) *γ-Methylheptan-ε-ol*, $CHMeEt\cdot CH_2\cdot CHEt\cdot OH$, a liquid with a mint-like odour, has b. p. 167—169° (corr.), D^0 0·8493; its *acetate* has b. p. 183—185° (corr.). On oxidation, the alcohol yields *γ-methylheptan-ε-one*, $C_8H_{16}O$, b. p. 161° (corr.); the *semicarbazone* crystallises in needles, m. p. 96°. The constitution of the foregoing alcohol and ketone was deduced from a study of their oxidation products.

(2) The dodecyl alcohol, "*tri*sec.-*butylic alcohol*," $C_{12}H_{26}O$, b. p. 250—255° (corr.), an agreeably smelling liquid, is converted on oxidation into the corresponding *ketone*, $C_{12}H_{24}O$, b. p. 247—248° (corr.). This forms a *semicarbazone*, m. p. 161—162°. W. O. W.

Methylacetenylcarbinol [Butinene-γ-ol]. Robert Lespieau (*Compt. rend.*, 1910, **150**, 113—114. Compare Abstr., 1908, i, 496).—A description of a method for preparing alcohols of the type $OH\cdot CHR\cdot C{:}CH$. *β-Bromo-Δ$^\alpha$-butene-γ-ol*, $OH\cdot CHMe\cdot CBr{:}CH_2$, obtained by the action of magnesium methyl iodide on bromoacraldehyde, is a colourless liquid, b. p. 59·5—60°/14 mm., or 151°/732 mm. (decomp.); it forms a *phenylurethane*, m. p. 62·5—63·5°. Alcoholic potassium hydroxide converts the alcohol almost quantitatively into acetylene, whilst the aqueous alkali brings about a more complex change. Amongst the products recognised were acetylene, propionic acid, and *butinene-γ-ol*, $OH\cdot CHMe\cdot C{:}CH$. This was isolated, not quite free from water, as a liquid, b. p. 107—109°/760 mm. By treating with an ammoniacal cuprous chloride solution, a precipitate is formed, which, on treatment with iodine and potassium iodide, is converted into *aaβ-tri-iodo-Δ$^\alpha$-butene-γ-ol*, $OH\cdot CHMe\cdot CI{:}CI_2$, m. p. 96°.

W. O. W.

Unsaponifiable Constituents of Japan Tallow. Hermann Matthes and W. Heintz (*Arch. Pharm.*, 1909, **247**, 650—657).—Japan tallow, m. p. 53—53·5, D 1·0032, is saponified by alcoholic potassium hydroxide, and the clear soap solution is diluted with water and extracted with ether. The residue obtained by the distillation of

the ethereal extract is submitted to a repetition of these operations. The final residue thus obtained in 0·68% yield is a yellowish-brown mass (iodine number 36·25), which is separated by petroleum into an insoluble portion, from which myricyl alcohol is isolated, and a soluble portion, from which phytosterol, m. p. 139°, and ceryl alcohol, m. p. 79°, are obtained, together with a saturated *alcohol*, m. p. 65° (*acetate*, m. p. 41°), which is probably nonadecyl alcohol, $C_{19}H_{40}O$.

C. S.

Dimethyldiethyldicarbinol [γδ - Dimethylhexane - γδ - diol]. Mlle. Cécile Frumina (*Bull. Acad. roy. Belg.*, 1909, 1151—1157).—Lawrinowitsch's pinacone, obtained by reducing methyl ethyl ketone with sodium (Abstr., 1877, ii, 427), has been prepared by the action of magnesium ethyl iodide on methyl oxalate, and proved to consist of a single liquid substance, γδ-dimethylhexane-γδ-diol,

$$OH\cdot CMeEt\cdot CMeEt\cdot OH,$$

b. p. 195°/760 mm. or 10°/110 mm. The solid modification obtained by Zelinsky and Krapiwin (Abstr., 1893, i, 390) in repeating Lawrinowitsch's experiment was not produced in the synthesis now described. The *diethyl ether* has b. p. 142—143°/760 mm. or 110—111°/20 mm., and is liquid. The *dichloride* boils at 165—166°/760 mm. or at 114—115°/18 mm. T. A. H.

Drying of Moist Ether. E. von Siebenrock (*Monatsh.*, 1909, 30, 759—766).—A comparative study of calcium chloride, potassium carbonate, sodium sulphate, magnesium sulphate, sylvite, potassium chloride, calcium sulphate, and carnallite, having regard to their use, in the anhydrous state, for the removal of water from moist ether. The first two substances mentioned are shown to be most efficacious; sodium sulphate, a substance frequently recommended and used for drying ether, is not very effective, and may be replaced with great advantage by carnallite and magnesium sulphate. W. H. G.

Action of Sulphur and Ammonia on Organic Sulphides and Disulphides. Bror Holmberg. (*Ber.*, 1910, 43, 220—226. Compare Abstr., 1908, i, 308).—Organic sulphides and disulphides form reddish-brown additive products of the general formula R_2S_x,yNH_3 with sulphur and ammonia. The reaction is reversible, the equilibrium depending on the sulphide used. In some cases, as with ethyl and *p*-tolyl disulphides, the additive product undergoes further change into the tetrasulphide, according to the equation:

$$R_2S_x,yNH_3 \rightleftarrows R_2S_4 + S_{x-4} + yNH_3,$$

so that the ammonia can be considered to act catalytically on the formation of tetrasulphides from disulphides and sulphur.

The organic sulphide or disulphide is dissolved in absolute alcohol, an excess of flowers of sulphur added, and the solution then saturated with ammonia, whereby the colour gradually changes to a dark brown. After some weeks the undissolved sulphur is collected and weighed, the filtrate allowed to evaporate spontaneously, and the residue then investigated.

With ethyl sulphide, the residue consisted of a minute trace of sulphur, but the additive product must have been formed in solution,

since the presence of ethyl sulphide is necessary for the formation of the brown colour.

Ethyl disulphide gave a residue of a yellow uncrystallisable oil; when this was distilled under diminished pressure (12 mm.), a colourless liquid distilled over at 77—78°, and the residue in the flask consisted of ethyl tetrasulphide.

p-Tolyl disulphide (prepared from *p*-tolyl mercaptan and sulphuryl chloride in ethereal solution, or by the spontaneous oxidation of an alkaline solution of the mercaptan) gave a solid residue, contaminated with oil, which after recrystallisation from alcohol is found to be a mixture of the di- and tetra-sulphide, the latter having m. p. 75°.

Diethyl dithiodiglycollate gave a dark-coloured solution, from which the original substances were always regenerated, no matter what the treatment; large quantities of sulphur dissolved. If the filtrate, after collecting the excess of sulphur, was again saturated with ammonia and kept for six weeks, the amide, m. p. 156—157°, derived from the original ester was formed.

In an appendix on the inorganic polysulphides, the author states his opinion that compounds with simple sulphur chains are colourless, or only pale yellow; a brown colour is due to the presence of larger atomic complexes, S_x. Whether the compound should be formulated as M_2S,S_x or M_2S_2,S_x is left undecided. T. S. P.

Crystalline Form and Optical Characters of Lead Formate. B. Karandéeff (*Centr. Min.*, 1910, 17—24).—Crystals of lead formate, $Pb(CHO_2)_2$, are orthorhombic, with $a : b : c = 0{\cdot}74538 : 1 : 0{\cdot}84656$. Detailed determinations of the optical constants are given. L. J. S.

[Electrolysis of Carboxy-acids.] Felix Kaufler (*Ber.*, 1910, 43, 266).—The statement made by the author and C. Herzog (Abstr., 1909, i, 870) in connexion with the attitude of Forster and Piguet (Abstr., 1904, i, 965) towards the superoxide theory was incorrect. An error was also made in the reference to the work of Miller and Hofer. R. V. S.

Formation of Dichloroacetic Acid from Trichloroacetaldehyde by Wallach's Method. Arthur Kötz (*Festschrift Otto Wallach*, 1909, 496—501. Compare Wallach, Abstr., 1878, 285, 288).—The conversion of chloral into dichloroacetic acid, which may be brought about through the agency of water alone, is greatly facilitated by the presence of potassium cyanide, probably owing to the intermediate formation of chloralcyanohydrin, $CCl_3{\cdot}CH(OH){\cdot}CN$, and $\alpha\alpha$-dichloro-β-cyano-β-hydroxyethylene, $CCl_2{:}C(OH){\cdot}CN$, or the tautomeride, dichloropyruvonitrile, $CHCl_2{\cdot}CO{\cdot}CN$. The following observations are quoted in support of this explanation: (1) Dichloroacetic acid is formed by the action of water on chloralcyanohydrin. (2) Nitriles of dihalogenated pyruvic acids under the conditions of Wallach's method yield dihalogenated acetic acids and hydrogen cyanide. (3) Trichlorolactic acid may be converted in aqueous solution into dichloroacetaldehyde, hydrogen chloride, and carbon dioxide;

this reaction undoubtedly takes place through the intermediate formation of αα-dichloro-β-hydroxyethylenecarboxylic acid or the tautomeric dichloropyruvic acid, since dihalogenated pyruvic acids decompose in aqueous solution, yielding dihalogenated aldehydes and carbon dioxide.

Chloroacetaldehyde and dichloroacetaldehyde behave similarly to chloral, with the difference that the first-named substance cannot be converted into formic acid and chloromethane.

β-Halogenated aldehydes, such as β-chloropropaldehyde, cannot be converted into the corresponding acids even under the influence of hydrogen cyanide; it would appear, therefore, that reactions of the nature under discussion only take place when halogen and oxygen are united to adjacent carbon atoms. W. H. G.

Catalytic Phenomena. Jacob Boeseken (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 417—421).—By the researches of Perrier (Abstr., 1900, i, 331) and the author (Abstr., 1900, i, 349; 1901, i, 474) it has been shown that in Friedel and Crafts' reaction it is not the aromatic hydrocarbon, but the chloride or anhydride, which is first attacked by the aluminium chloride, as in many cases additive products can be isolated. The author regards this initial action as consisting of a loosening of the chloride, and possibly also of the double linkings of the benzene derivative, it being known that many reactions indicate the action of aluminium chloride to be purely a dissociating one. In order to test this view, the author has examined several additional cases, and with the idea that the reaction might proceed more readily if stable chlorine compounds, such as hydrogen chloride, could be formed during the decomposition, the substances chosen were trimethylacetyl chloride, dichloroacetyl chloride, chloral and trichloroacetyl chloride; these all contain a more or less overloaded carbonyl group, so that the reaction could be followed by the evolution of carbon monoxide. The results obtained are as follows: Trimethylacetyl chloride is resolved at 0° according to the equation $CMe_3 \cdot COCl = HCl + CO + C_4H_8$, the *iso*butylene being almost entirely polymerised. When gently heated, chloral undergoes decomposition in two directions: (*a*) $CCl_3 \cdot CHO = HCl + CO + CCl_2$ (or C_2Cl_4), to the extent of 70—75%; and (*b*) $CCl_3 \cdot CHO = CO + CHCl_3$. With dichloroacetyl chloride decomposition takes place in the two directions: $CHCl_2 \cdot COCl = CO + CHCl_3$, to 60%, and $CHCl_2 \cdot COCl = CO + HCl + CCl_2$, the CCl_2 presumably being polymerised to C_5Cl_{10}. Trichloroacetyl chloride, when repeatedly distilled with aluminium chloride, is decomposed in one direction: $CCl_3 \cdot COCl = CCl_4 + CO$.

It is remarkable that, in spite of its excess of chlorine atoms, trichloroacetyl chloride is the most difficult of attack. The reaction seems to proceed particularly smoothly in the case where hydrogen and chlorine atoms are united with two adjacent carbon atoms.

The course of the reaction with chloral and dichloroacetyl chloride indicates that it is the movable chlorine atom which is initially rendered active. The action of aluminium chloride on trimethylacetyl chloride is too violent to admit of the first stage of the reaction being ascertained. But with sulphuric acid, which in many cases

behaves analogously to aluminium chloride and forms the same kind of additive products, the reaction appears to pass through the phases: $CMe_3 \cdot COCl + H_2SO_4 = CMe_3 \cdot CO \cdot SO_4H + HCl$ and $CMe_3 \cdot CO \cdot SO_4H = H_2SO_4 + CO + C_4H_8$, the chlorine atom being first detached by the sulphuric acid. T. H. P.

Detergent Action of Soap Solutions. III. Walthère Spring (*Bull. Acad. roy. Belg.*, 1909, 1059—1065; *Arch. Sci. phys. nat.*, 1910, [iv], 29, 42—48, and *Bull. Soc. chim. Belg.*, 1910, 24, 17—54.* Compare Abstr., 1909, i, 628, and this vol., i, 6).—The results obtained with "red ochre" (*loc. cit.*) have led to the extension of this investigation to the action of hydrated alumina on soap solutions. The results are analogous to those obtained with red ochre.

To each member of a series of fourteen solutions containing quantities of soap ranging from 1/2·5% to 1/16%, 2 c.c. of a mixture of water and aluminium hydroxide (equivalent to 0·0061% Al_2O_3) were added. The mixtures containing 1/8% and 1/16% of soap flocculated in twenty-four hours, and that containing 1/4% of soap flocculated in thirty-nine hours; the remaining mixtures, except that containing 1/2·5% soap, having in this time flocculated partially. Changes in the relative proportions of aluminium hydroxide and soap displace these points of flocculation, and also mask the periodicity. The coagulated product is pulverulent, like that obtained with ferric hydroxide (*loc. cit.*), and on ignition gives a mixture of about 3 mols. of alumina to 1 mol. of sodium carbonate, indicating an original adsorption product of 3 mols. of alumina with 2 of soap. T. A. H.

Detergent Action of Soap Solutions. IV. Walthère Spring (*Bull. Acad. roy. Belg.*, 1909, 1128—1139, and *Bull. Soc. chim. Belg.*, 1910, 24, 17—54*).—Silicic acid, clay, and cellulose react with soap solutions in the same way as lampblack (Abstr., 1909, i, 628), red ochre (this vol., i, 6) and alumina (preceding abstract) forming with a part of the soap insoluble adsorption compounds, which are less adhesive than the original colloidal substances.

A soap solution in which silicic acid has been suspended, and which has been clarified by deposition, does not redden with phenolphthalein solution, and yields less alkaline ash on evaporation and ignition than the original solution, due to combination of the silicic acid with a basic portion of the soap. Such a suspension on filtration yields a filtrate containing silica, and the amount of the latter in the filtrate augments with the diminution in concentration of the soap solution (compare *loc. cit.*). Solutions of soap of strengths varying from 1/512% to 2% show periodicity in suspending power for silicic acid, the maxima being at about 1/16% and 1/2%, and the minimum at about 1/8%.

Pottery clay behaves in a similar manner. Its suspension in soap solution of any strength clears with difficulty, but a maximum suspending power is shown by a soap solution of 1/8% strength. After ignition, the clay decomposes soap less readily, and deposits much more easily from suspensions, the maximum suspending power for baked clay being shown by a soap solution of 1/32% strength.

* The last reference contains the complete paper, Parts I—IV.

Cellulose has no effect on soap in solutions containing less than 1%, but for concentrations above this the soap is decomposed, a basic portion combining with the cellulose. T. A. H.

Xanthic Acid and Dixanthogen [Ethyl Di-oxythiocarbonate]. II. Manfred Ragg (*Chem. Zeit.*, 1910, **34**, 82—84. Compare Abstr., 1908, i, 604).—A pure xanthate can only be prepared when water is excluded from the reaction mixture in order to prevent hydrolysis. To prepare sodium xanthate, sodium is dissolved in excess of ethyl alcohol, and then the calculated quantity of carbon disulphide added, the reaction mixture being stirred and cooled meanwhile. The solution so obtained is fairly stable, and gives a yellow precipitate with copper salts which is free from the dark brown impurities which are formed when hydrolytic products are present. The yellow precipitate consists of cuprous xanthate and ethyl di-oxythiocarbonate, the reaction taking place quantitatively according to the equation: $4NaS{\cdot}CS{\cdot}OEt + 2CuSO_4 = Cu_2(S{\cdot}CS{\cdot}OEt)_2 + S_2(CS{\cdot}OEt)_2 + 2Na_2SO_4$. The dixanthogen can be extracted from the precipitate by means of carbon tetrachloride. It is noteworthy that if sodium is added to a mixture of ethyl alcohol and carbon disulphide, sodium xanthate is not formed, but a compound which gives a dark red precipitate with copper salts, and only changes into yellow cuprous xanthate on warming.

The following dixanthogens [di-oxythiocarbonates] and xanthates have been prepared in a similar manner from the corresponding alcohols:

Methyl di-oxythiocarbonate, $S_2(CS{\cdot}OMe)_2$, is a brownish-yellow, viscid oil, with an odour different from that of the ethyl compound, and somewhat similar to that of acetone; D = 1·180; b. p. 122° (decomp.). *Cuprous methyl xanthate* is a pale yellow powder.

n-*Propyl di-oxythiocarbonate*, $S_2(CS{\cdot}OPr)_2$.—Brown liquid with no characteristic odour; D = 1·087; b. p. 117° (with decomposition). *Cuprous* n-*propyl xanthate* forms a pale yellow powder.

iso*Butyl di-oxythiocarbonate*, $S_2(CS{\cdot}O{\cdot}C_4H_9)_2$, is a yellow oil; D = 1·080; b. p. 165°. In the preparation of sodium *iso*butyl xanthate, it is necessary to use a large excess of the alcohol and to warm the reaction mixture. After the addition of the copper salt, the excess of *iso*butyl alcohol must be extracted with 40% ethyl alcohol, in which both the cuprous xanthate and the dioxythiocarbonate are insoluble. *Cuprous* iso*butyl xanthate* is a light yellow powder.

Amyl di-oxythiocarbonate, $S_2(CS{\cdot}O{\cdot}C_5H_{11})_2$, was prepared from ordinary commercial amyl alcohol. Dark yellow oil; D = 1·007; b. p. 158°. *Cuprous amyl xanthate* is pale yellow in colour.

Benzyl di-oxythiocarbonate, $S_2(CS{\cdot}O{\cdot}C_7H_7)_2$.—Yellow oil with a characteristic, but not unpleasant odour; D = 1·218. *Cuprous benzyl xanthate* is coloured pale yellow, and is stable up to 60°. *Sodium benzyl xanthate* can be recrystallised from alcohol, but the aqueous solution gradually decomposes.

Attempts to prepare glycerol derivatives were unsuccessful, although the results obtained point to the existence of a cuprous glyceryl monoxanthate. T. S. P.

Addition of Acid Anhydrides to Aldehydes and Ketones. Rudolf Wegscheider and Ernst Späth (*Monatsh.*, 1909, **30**, 825—869).—Acid anhydrides, for example, the anhydrides of acetic acid, propionic acid, chloroacetic acid, and benzoic acid, react with aldehydes in the presence of sulphuric acid, yielding di-esters of the aldehyde hydrates; of all the aldehydes investigated, citronellal alone did not behave in this manner, owing to the extreme readiness with which it is decomposed by acids. In the absence of sulphuric acid and at high temperatures, esters of the enolic form of the aldehyde are chiefly formed (compare Semmler, Abstr., 1909, i, 364). The mode of action of the sulphuric acid is not clear; that the mixed anhydride which is possibly formed is directly concerned in the esterification of the aldehyde is not probable, for the sulphuric acid may be replaced by hydrochloric acid, in which case the mixed anhydride is acetyl chloride, but acetyl chloride reacts with aldehydes, yielding acetates of chlorinated alcohols and only very small quantities of aldehyde diacetates. The sulphuric acid may likewise be replaced by nitric acid, phosphoric acid, or oxalic acid, but not by 3-nitrophthalic acid, although this is a stronger acid than oxalic acid; possibly the acid, in this case, is converted into the anhydride, and is thus replaced by acetic acid.

Attempts to acetylate acetone, acetophenone, and benzophenone have proved unsuccessful.

The aldehyde diacetates are hydrolysed quite readily by hot water, and are decomposed by phenylhydrazine, with the formation of aldehyde phenylhydrazones and *αβ*-acetylphenylhydrazine. The dibenzoates are hydrolysed by hot, but not by cold, aqueous potassium hydroxide.

Certain of the compounds mentioned later are extremely poisonous.

The following compounds, all of which have been prepared by various investigators in different ways, are readily obtained by the interaction of the aldehyde and acid anhydride under the influence of sulphuric acid: methylene diacetate, ethylidene diacetate, heptylidene diacetate, chloral diacetate, crotonaldehyde diacetate, cinnamylidene diacetate, ethylidene dipropionate, chloral bischloroacetate, b. p. 168°/10 mm. (compare Gabutti, Abstr., 1900, i, 370), and methylene dibenzoate. The interaction of salicylaldehyde and acetic anhydride in the presence of sulphuric acid leads to the formation of *o*-acetyloxybenzaldehyde diacetate; salicylaldehyde diacetate is not formed, as stated by Perkin (*Annalen*, 1868, **146**, 371), neither could it be obtained in the manner described by Barbier (Abstr., 1880, 468).

Propylidene diacetate, $C_7H_{12}O_4$, is a colourless liquid, b. p. 184—185° (corr.); iso*butylidene diacetate*, $C_8H_{14}O_4$, is a liquid with a not unpleasant odour, b. p. 189° (corr.); *benzylidene dipropionate*, $C_{13}H_{16}O_4$, is an oil, b. p. 158—159°/10 mm.; *chloral dibenzoate*, $C_{16}H_{11}O_4Cl_3$, forms large, well-defined, glistening crystals, m. p. 63—65°; *benzylidene dibenzoate*, $C_{21}H_{16}O_4$, crystallises in long, silky needles, m. p. 61—62°; o-*nitrobenzylidene dibenzoate*, $C_{21}H_{15}O_6N$, is dimorphous, m. p. 123—124° and 147—148°; it decomposes when distilled in a vacuum, yielding *o*-nitrobenzaldehyde and benzoic acid; m-*nitro benzylidene dibenzoate* forms rosettes of silky, white crystals, m. p.

97—99°; the *para*-isomeride has m. p. 118°; *cinnamylidene dibenzoate*, $C_{23}H_{18}O_4$, crystallises in needles, m. p. 133—135°.

Ethylidene dibenzoate, $C_{16}H_{14}O_4$, could not be prepared by the sulphuric acid method; it is obtained by the action of benzoic anhydride on ethylidene diacetate in the presence of a small quantity of sulphuric acid at 100°, and forms small, glistening crystals, m. p. 70—71°. W. H. G.

Vicianose, a New Reducing Sugar Containing C_{11}. Gabriel Bertrand and Gustave Weisweiller (*Compt. rend.*, 1910, **150**, 180—182. Compare Abstr., 1906, i, 68; 1908, i, 817).—The cyanogenetic glucoside observed by Bruyning (Abstr., 1900, ii, 160) in the seeds of *Vicia angustifolia* undergoes hydrolysis when treated with a diastase occurring in the seeds. A new sugar, *vicianose*, $C_{11}H_{20}O_{10}$, has been isolated from the products of hydrolysis. This is the first biose isolated from a glucoside. The compound crystallises in spherular aggregates of small needles; it is very soluble in water, but only sparingly so in alcohol. A 10% aqueous solution, after fifteen minutes, shows $\alpha_D^{20-22}+15{\cdot}8°$ (300 mm. tube), but after twenty-two hours the rotation remains constant at $\alpha_D^{20}+9{\cdot}32°=[\alpha]_D+39{\cdot}72°$. Vicianose has m. p. about 210°; it has a somewhat higher cupric reducing power than maltose, and is not fermented by yeast. W. O. W.

Theory of the Nitration of Cellulose. Alexis V. Saposchnikoff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1712—1741. Compare Abstr., 1907, i, 390).—The author first discusses the work of previous investigators on the action of nitric acids of various concentrations, either alone or mixed with sulphuric acid, on cellulose.

The non-homogeneity of nitro-cellulose is due largely to the dilution of the nitrating mixture by the water developed in the reaction, the external parts of the mass being more highly nitrated than the inner parts. The final degree of nitration is influenced by the reversibility of the process. If the nitric acid employed is sufficiently concentrated to form nitric ethers of cellulose, and if it is in sufficiently great excess, chemical action proceeds very rapidly. Thus, with a mixture containing 23·8% HNO_3, 71·5% H_2SO_4, and 4·7% water at 20°, it was found that, after two minutes, only 1·8% of the cellulose (cotton) remained unattacked, the nitrated part containing 12·7% of nitrogen, corresponding with the introduction of $10NO_3$; after five minutes, $11NO_3$ were introduced. These results, together with those obtained with a nitrating mixture composed of 30% HNO_3, 65% H_2SO_4, and 5% H_2O, are in accord with those obtained by Lunge and Bebie (Abstr., 1901, i, 508).

Ternary mixtures of sulphuric and nitric acids and water were investigated by determining the densities, electrical conductivities, and partial pressures of the vapours of nitric acid in the mixtures (compare Abstr., 1904, ii, 251, 558, 614; 1905, ii, 583). The results obtained indicate that in such mixtures there occurs a reversible process of the type: $HNO_3,nH_2O+H_2SO_4 \rightleftharpoons HNO_3,(n-x)H_2O+H_2SO_4,xH_2O$. This dehydration of nitric acid reaches a limit with a mixture of the composition corresponding with the equation:

$$HNO_3+xH_2SO_4+xH_2O=HNO_3+x(H_2SO_4,H_2O),$$

further addition of sulphuric acid resulting in the formation of nitric anhydride. The results of the investigation of these ternary mixtures are given in the form of a triangular diagram (compare Abstr., 1907, i, 390).

The relation between the composition of the nitrating mixture and the degree of nitration of cellulose is discussed with the help of a large number of numerical results. T. H. P.

Synthesis of the Phospho-organic Acid of the Seeds of Plants (Posternak's Anhydroxymethylene-diphosphoric Acid). Angelo Contardi (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 23—27).—By the interaction of inosite and phosphoric acid in a current of carbon dioxide, the author has prepared an acid, $C_6H_{18}O_{24}P_6$, which exhibits all the physical and chemical characters of the phospho-organic acid obtained from the seeds of plants (compare Abstr., 1909, i, 203). By treating its barium or calcium salt with cupric and sodium acetates, the salt $C_6H_6O_{24}Cu_4Ba_2$ or $C_6H_6O_{24}Cu_4Ca_2$ is obtained, whilst the calcio-magnesium salt agrees in chemical and physical properties with the corresponding derivative of the phytin extracted from rice bran (*loc. cit.*). On hydrolysis, the acid yields compounds poorer in phosphorus, one of which, *inosite-diphosphoric acid*, $C_6H_{14}O_{12}P_2$, was isolated as a white, deliquescent, vitreous mass, and its *barium* salt, $C_6H_{10}O_{12}P_2Ba_2$, prepared and analysed. T. H. P.

Phosphoric Acid Esters of Carbohydrates. I. On Sucrose-phosphoric Acid. Carl Neuberg and H. Pollak (*Biochem. Zeitsch.*, 1910, **23**, 515—517).—Sucrose in water, freshly prepared calcium oxide, phosphoryl chloride, and dry chloroform were kept together at the temperature of melting ice, and the following reaction took place :

$2C_{12}H_{22}O_{11} + 2POCl_3 + 5CaO = 3CaCl_2 + H_2O + 2C_{12}H_{12}O_{10}{\cdot}O{\cdot}PO_3Ca$.

The sucrose-phosphate of calcium was separated out and analysed ; it is a fine, white powder, readily soluble in water. The entrance of phosphoric acid into the sucrose molecule completely abolishes its fermentability. W. D. H.

Lipoproteins and the meaning of Fatty Degeneration in Cells. V. Further Syntheses of Lipopeptides. VI. Further Researches on the Cleavage of Lipopeptides. S. Bondi and Franz Eissler (*Biochem. Zeitsch.*, 1910, **23**, 499—509, 510—513. Compare Abstr., 1909, i, 458, 459).—In continuation of former work, and by the use of the same methods, the following were prepared : Butyrylglycine, m. p. 70°. Butyrylalanine, thin prisms, m. p. 88—93° ; its *ethyl* ester has b. p. 135—145°/14 mm. Butyrylalanylglycine, thin prisms, m. p. 171°. Palmitylalanylglycine, needles, m. p. 128—138°, not sharp. Laurylalanylglycine, groups of needles, m. p. 141°. *iso*Valerylglycine, thin prisms, m. p. 87—90. Laurylpeptone, crystalline. Palmitylpeptone, a brownish-yellow powder. Witte's peptone was used in the preparation of the two last-named substances. Unlike proteins and nearly all non-aromatic amino-acids, they are all readily soluble in alcohol. They are insoluble in light petroleum, and almost so in ether.

Butyrylglycine is not resolved by pepsin or trypsin, but is by an extract of autolysed kidney; butyrylalanine is only slightly decomposed by a similar extract of liver. Trypsin has also no action on butyrylalanylglycine or laurylalanylglycine. The latter substance, however, is decomposed by autolysed kidney extract. No evidence of reversible action was found. W. D. H.

A New Method of Forming *iso*Cyanates [Carbimides] and Hofmann's Thiocarbimide Reaction. II. Richard Anschütz (*Annalen*, 1910, 371, 201—226. Compare Abstr., 1908, i, 326).—The behaviour of the mercuric and chloromercuric salts of ethylthiolcarbamic acid and *iso*butylthiolcarbamic acid when heated alone, likewise the decomposition of mercuric and chloromercuric ethyldithiocarbamates by boiling water and by heat alone, has been investigated quantitatively, with the result that the conclusions published previously (*loc. cit.*) have to be modified slightly.

Chloromercuric ethylthiolcarbamate when heated decomposes thus: $3NHEt\cdot CO\cdot SHgCl \longrightarrow Hg_3S_2Cl_2 + COS + 2EtNCO + NH_3EtCl$; in this way it is possible to prepare alkylcarbimides without difficulty. The corresponding ethyldithiocarbamate is decomposed by heat analogously.

Mercuric ethylthiolcarbamate when heated alone decomposes into red mercuric sulphide, carbonyl sulphide, and *s*-diethylcarbamide; the formation of hydrogen sulphide could not be detected, owing to the readiness with which it interacts with ethylcarbimide, yielding carbonyl sulphide and *s*-diethylcarbamide. Mercuric ethyldithiocarbamate, when similarly treated, decomposes in two ways, represented by the equations: $[NHEt\cdot CS\cdot S]_2Hg \longrightarrow$ (1) $HgS + CS_2 + CS(NHEt)_2$ or (2) $HgS + H_2S + 2EtNCS$; the mercuric sulphide obtained in these reactions is black. The extent to which the reaction represented by (2) takes place depends on the rate of heating, for hydrogen sulphide and ethylthiocarbimide interact, yielding carbon disulphide and *s*-diethylcarbamide. The salt undergoes the same change when boiled with water, but to a greater extent (about 50%) in the manner indicated by (2). In the preparation of alkylcarbimides by Hofmann's method, however, an excess of mercuric chloride is employed; this results in the formation of chloromercuric ethyldithiocarbamate, which is decomposed by boiling water, thus: $NHEt\cdot CS\cdot SHgCl = HgS + SCNEt + HCl$.

The *iso*butyl salts undergo the same changes as the analogous ethyl compounds.

Chloromercuric ethyldithiocarbamate is prepared by adding an aqueous solution of ethylammonium ethyldithiocarbamate to a cold solution of mercuric chloride in acetone; it crystallises in white leaflets. W. H. G.

Ethyl Oxalosuccinonitrile and Diethyl Dioxalosuccinonitrile. Wilhelm Wislicenus and Heinrich Elvert (*Ber.*, 1910, 43, 228—234. Compare Abstr., 1908, i, 965).—Ethyl oxalosuccinonitrile has m. p. 112—113°, not 102—103° as previously stated. A better yield is obtained if the method of preparation formerly given is modified

so as to ensure the presence of an excess of succinonitrile throughout the reaction. According to observations made by A. Hantzsch and H. Ley, alcoholic solutions of the β-form fluoresce. H. Ley and von Engelhardt find that 0·005N-alcoholic solutions of the α-form also fluoresce, but the fluorescence disappears when an excess of sodium ethoxide is added, so that it is due to the presence of a small proportion of the β-form.

By doubling the quantities of ethyl oxalate and potassium ethoxide taken, and reversing the order of addition in the method formerly described for the preparation of ethyl oxalosuccinonitrile, the *dipotassium* salt of *diethyl dioxalosuccinonitrile* may be obtained (compare Michael, Abstr., 1903, i, 736). The substance gives a deep reddish-brown coloration with ferric chloride, and ammonia is evolved when it is boiled with ammonium chloride. On acidifying its aqueous solution, the *monopotassium* salt is precipitated. It forms small, lustrous needles, m. p. above 140° (decomp.), and gives a red coloration with ferric chloride. Copper acetate yields with both potassium salts and with the free nitrile the same *monocopper* salt, in the form of small green needles, which become brown at 170°, and melt at 220—225°. By acidifying an aqueous solution of the potassium salt, the *enolic* form of *diethyl dioxalosuccinonitrile* may be obtained as a viscous, brown oil, which, on shaking with water, yields a hydrate which forms colourless needles, m. p. 52—53°, gives a weak red coloration with ferric chloride, and is probably the *dihydrate*. It readily loses water, forming the *monohydrate*, m. p. 102—104°. This hydrate also gives a weak red coloration with ferric chloride. The enolic form and its hydrates change spontaneously into the ketonic form, which crystallises in yellow prisms, m. p. 123—124° (Michael, *loc. cit.*). The alcoholic solutions of this substance do not fluoresce. It is probably a ketonic enol of the constitution :

$$CO_2Et\cdot CO\cdot CH(CN)\cdot C(CN):C(OH)\cdot CO_2Et.$$

R. V. S.

Carbon Subnitride, C_4N_2. Charles Moureu and J. Ch. Bongrand (*Compt. rend.*, 1910, 150, 225—227).—This substance has been obtained by the elimination of $2H_2O$ from acetylenedicarboxylamide,

$$NH_2\cdot CO\cdot C{:}C\cdot CO\cdot NH_2;$$

it may therefore be regarded as dicyanoacetylene, NC·C:C·CN. The analysis of the compound presented difficulties, but it has been shown to contain less than 0·6% of hydrogen. Carbon subnitride occurs as slender, colourless needles, m. p. 20·5—21°, b. p. 76°/753 mm., D_4^{25} 0·9703. The vapour is powerfully irritant, and has an odour resembling that of cyanogen; at 130° it is spontaneously inflammable in air, burning with a flame like that of cyanogen. The molecular refractions for the D-sodium line and for the α-, β-, and γ-hydrogen lines have been determined : M_D 21·641 ; M_γ—M_α 1·023. Refraction and dispersion are considerably higher than the values calculated on the assumption that the compound has the foregoing constitution (compare Abstr., 1906, ii, 1), probably through the contiguity of the three triple linkings.

The vapour density between 56° and 184° is in agreement with the formula C_4N_2. W. O. W.

Naphthene Formation. IV. Formation of Naphthene from Olefines and from Artificial Lubricating Oil and the Synthesis of the Latter. Carl Engler and O. Routala (*Ber.*, 1910, 43, 388—397).—The conversion of olefines into naphthenes does not, as a rule, take place directly. Probably, in the first place, polymerisation to polyolefines takes place, and these, on account of their content of labile hydrogen atoms, yield, firstly, paraffins, and subsequently decompose into naphthenes, on the one hand, and lubricating oils, on the other.

When the decomposition is carried out at low temperatures, for example, with aluminium chloride at the ordinary temperature, or at the boiling point of amylene, relatively little naphthene is formed along with paraffins and lubricating oil; at higher temperatures relatively more naphthene is formed, and the lubricating oils in part decompose, forming naphthene.

When amylene is heated in tubes under pressure, methane and hydrogen are formed. By the action of aluminium chloride on amylene in the cold, an oil is formed containing more than 87% of carbon, having the composition C_nH_{2n-6}, and agreeing in composition and properties with natural lubricating oil.

When heated for some time at 350°, the lubricating oil gives rise to a mixture of unsaturated and saturated hydrocarbons; the lower boiling fractions are in the main homologues of methane, the higher boiling fractions contain increasing proportions of naphthenes.

E. F. A.

Naphthene Formation. V. The Products of Heating Cylinder Oil Under Pressure. Carl Engler and B. Halmai (*Ber.*, 1910, 43, 397—405).—Large quantities of a Baku cylinder oil were heated from four to six hours under pressure at 400—430°. The product (b. p. 25—250°) was carefully fractionated, and the constituents of the successive fractions identified. The earlier fractions contained almost entirely paraffin hydrocarbons; as the boiling point rose, the proportion of naphthenes present increased. The highest boiling fractions consisted of lubricating oils, which behaved in a similar manner to the natural oils and those synthesised from amylene.

E. F. A.

Naphthene Formation. VI. Possible Formation of Hydrocarbons in Nature, and the Origin of the Optical Activity of Petroleum. Carl Engler (*Ber.*, 1910, 43, 405—411. Compare preceding abstracts).—In nature, bituminated animal and plant residues break down into solid paraffins, olefines, and liquid paraffins. The effect of heat and pressure, in conjunction with long periods of time, causes the solid paraffins to break down into liquid paraffins and olefines. The olefines condense to polyolefines; this gives rise to liquid paraffins, naphthenes, and lubricating oils; the last at a still higher temperature undergo further decomposition into liquid paraffins, naphthenes, and lubricating oils with less hydrogen. None of these changes is reversible. They take place simultaneously, and no great heat is required if the period of time be long enough. The petroleums

which have been exposed to the highest temperature contain most naphthenes and lubricating oils, although they may be younger in the geological sense than oils which contain mostly paraffins and have been exposed to lower temperatures.

The explanation given is in agreement with the fact that oils rich in naphthenes are usually rich in lubricating oils and vice versâ. The higher boiling fractions of the heated natural cylinder oil (see previous abstract) still preserve some optical activity, and it would appear that the optically active constituents of petroleum oppose great resistance to racemisation by heat. Inasmuch as the heat in the natural process is probably less than that used experimentally, the fact that the natural petroleums are optically active is not in opposition to the combined heat and pressure theory of their formation. E. F. A.

Relation between Colour and Constitution. Iwan Ostromislensky (*Ber.*, 1910, 43, 197—198).—A claim for priority. Werner's observations on nitro-compounds and his deductions therefrom (this vol., i, 20) had been made by the author in a paper sent to, but not published by, the German Chemical Society. C. S.

Hydrocarbons from Cinnamyl Chloride, $CHPh{:}CH{\cdot}CH_2Cl$. Hans Rupe and J. Bürgin (*Ber.*, 1910, 43, 172—178).—Cinnamyl chloride, prepared by the action of hydrogen chloride gas on cinnamyl alcohol (compare Emde, Abstr., 1909, i, 708), is a mobile liquid, b. p. 116—117°/12 mm., solidifying to large, colourless needles, m. p. 8—9°. *Cinnamyl bromide* is obtained on heating cinnamyl alcohol with phosphorus tribromide in benzene solution in colourless needles, m. p. 30°, b. p. 130°/10 mm.

Cinnamyl chloride reacts with magnesium in ethereal solution; the product when decomposed with water yields a mixture of two hydrocarbons.

aζ-Diphenyl-$\Delta^{a\varepsilon}$*-hexadiene*, $CHPh{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CHPh$, forms thin, irregular, colourless, lustrous plates, m. p. 82°, b. p. 211°/11 mm., which in solution show a reddish-blue fluorescence. It yields a *tetrabromide*, separating in colourless, feathery needles, m. p. 194°.

aδ-Diphenyl-Δ^{a}*-hexene*, $CHEtPh{\cdot}CH_2{\cdot}CH{:}CHPh$, is a colourless, mobile fluid, b. p. 190°/11 mm., D^{20} 0·9915, n_D^{20} 1·588; the *hydrobromide* is a dark viscid oil. The constitution is indicated by the fact that, on oxidation with potassium permanganate, benzoic acid and phenylsuccinic acid are formed.

γ-Chloro-α-phenylpropane could not be prepared. *γ-Bromo-α-phenylpropane* is obtained by the action of phosphorus tribromide on hydrocinnamyl alcohol; the colourless liquid has b. p. 109°/11 mm. The bromide interacts with magnesium, forming propylbenzene and diphenylhexane. E. F. A.

Mobility of the Hydrogen Atoms of the Methylene Group in Compounds of the General Formulæ $R{\cdot}SO_2{\cdot}CH_2{\cdot}CN$, $R{\cdot}SO_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, $R{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2Et$. Julius Tröger and E. Lux (*Arch. Pharm.*, 1909, 247, 618—649).—The

close analogy between β-sulphonecarboxylic acids and β-ketonic acids, studied by Rössing (Abstr., 1890, 781) and Engelhardt (*J. pr. Chem.*, 1889, [ii], 40, 540) and further illustrated by Michael and Comey by the preparation of the sodium and alkyl derivatives of the former (Abstr., 1884, 319; 1885, 906; 1890, 781), suggests that the groups RSO_2 and CO_2Et exert the same influence as the groups RCO and CO_2Et on the neighbouring methylene group. The mobility of the methylene hydrogen atoms in arylsulphoneacetonitriles has already been shown to some extent by Tröger and Hillē (Abstr., 1905, i, 336), whilst the similar behaviour of such nitriles and phenylacetonitrile with amyl nitrite and sodium ethoxide and with aldehydes and sodium hydroxide has been manifested by Tröger and Prochnow (Abstr., 1908, i, 798). The present paper deals with the influence on the methylene hydrogen atoms of compounds $RSO_2\cdot CH_2X$ exerted by different groups X (where $X = CO_2R$, $CO\cdot NH_2$, or CN), the case of arylsulphonated acetamides being of special interest, since Tröger and Lindner (Abstr., 1908, i, 633) have shown that the methylene hydrogen atoms of the corresponding arylsulphonated thioacetamides are not replaceable by alkali metals or alkyl groups. The results of experiments on arylsulphonated acetonitriles, amides, and esters with alkalis, alkyl halides, aldehydes, and amyl nitrite and sodium ethoxide show that in these compounds the group $CO\cdot NH_2$ does not act like CN, and exerts an influence similar to, but weaker than, that of the group CO_2Et. For example, with alkalis, arylsulphonated acetic acids yield carbon dioxide and sulphones; their esters yield disodium derivatives; arylsulphonated acetamides are insoluble in sodium hydroxide, and arylsulphonated acetonitriles, although soluble in dilute sodium hydroxide, are not hydrolysed even by boiling, this only being effected by concentrated hydrochloric acid under pressure. The action of alkali and alkyl halides on

$$RSO_2\cdot CH_2\cdot CO_2Et$$

leads, as is known, to the formation of mono- and di-alkyl derivatives, on $RSO_2\cdot CH_2\cdot CN$ only to the production of dialkyl derivatives, and on $RSO_2\cdot CH_2\cdot CO\cdot NH_2$ results in simple hydrolysis by the alkali.

Amyl nitrite and sodium ethoxide simply hydrolyse arylsulphonated acetic esters, but react smoothly with the amides and nitriles to form *iso*nitroso-compounds by replacement of the methylene hydrogen atoms. The compounds obtained from the nitriles have the formula

$$RSO_2\cdot C(:NOH)\cdot CN,$$

and the following oximes and their derivatives are described; the *sodium* and *silver* salts are yellow powders, and the *lead* salts yellowish-white powders.

R.	m. p.	Methyl ether, m. p	Benzyl ether, m. p.	Benzoyl derivatives, m. p.	Acetyl derivatives, m. p.
Ph	—	57°	75°	153°	91°
p-C_6H_4Me	—	99	90	—	—
p-C_6H_4Cl	147°	115	80	162	126
p-C_6H_4Br	—	125	98	171	149
p-C_6H_4I	171	125	129	175	166
$OMe\cdot C_6H_4$	152	94	102	—	—
$OEt\cdot C_6H_4$	147	87	97	—	—

The following compounds, $RSO_2\cdot C(:NOH)\cdot CO\cdot NH_2$, are obtained in

a similar way, but less readily from arylsulphonated acetamides; the figures are m. p.'s: R = Ph, 153° (decomp.); R = *p*-C_6H_4Cl, 155° (decomp.); R = *p*-C_6H_4Br, 152° (decomp.); R = *p*-C_6H_4I, 178° (decomp.); the *sodium*, *silver*, and *lead* salts have been prepared.

Tröger and Prochnow (*loc. cit.*) have shown that arylsulphonated acetonitriles, like phenylacetonitrile, readily condense with certain aromatic aldehydes in the presence of a little sodium hydroxide. Arylsulphonated acetamides or acetic esters do not condense with aldehydes as a rule, but from salicylaldehyde the same compounds, $RSO_2\cdot C(CO)(CH\cdot C_6H_4)>O$, are obtained by loss of water and ammonia and water and ethyl alcohol respectively. Of such compounds, the following are mentioned: R = Ph, 219°; R = *p*-C_6H_4Cl, 243°; R = *p*-C_6H_4Br, 244°; R = *p*-C_6H_4I, 248°.

The bromination of arylsulphonated acetic acids, esters, and amides does not proceed smoothly, but the nitriles yield compounds,

$$RSO_2\cdot CBr_2\cdot CN,$$

which are also obtained by the action of bromine on the sodium salts of the corresponding oximes: R = Ph, 123°; R = *p*-C_6H_4Cl, 126°; R = *p*-C_6H_4Br, 129°; R = *p*-C_6H_4I, 131°. C. S.

Aniline Antimonyl Tartrate. Paul Yvon (*Compt. rend.*, 1910, **150**, 283—285).—Clarke's salt, $C_4H_5O_6(SbO)\cdot C_6H_7N$ (Abstr., 1882, 1051), separates with 1 mol. H_2O when allowed to crystallise from an aqueous solution at 15°; the crystals deposited at 35° are anhydrous. The hydrated salt forms stellate clusters of long prisms, which become opaque on exposure, losing water of crystallisation.

In 2—5% aqueous solution, the anhydrous salt has $[\alpha]_D^{17}$ 121·28°, D^{18} 2·112; one gram of the substance is soluble in 6·36 grams of water at 15°. The hydrate has $[\alpha]_D^{19}$ 115·61°, D^{20} 1·569.

The solubilities in water and alcohol at different temperatures are given, and also crystallographic details of the anhydrous salt.

W. O. W.

Complex Compounds of Aluminium Bromide with Organic Compounds. Iwan A. Kablukoff and Al. Sachanoff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1755—1762. Compare Menschutkin, Abstr., 1909, i, 897, 900).—Investigation of the melting-point curves of mixtures of aluminium bromide with benzene, toluene, xylene, naphthalene, dibromomethane, bromobenzene, and *p*-dibromobenzene indicates either a slight tendency of these organic compounds to give double compounds with aluminium bromide, or the extreme instability of such complex compounds. It seems, indeed, that for stable compounds to be formed with aluminium bromide, the presence of oxygen or nitrogen in the organic component is a necessary condition.

With aniline, four compounds are formed by aluminium bromide: $Al_2Br_6,2NH_2Ph$, m. p. 90°; $Al_2Br_6,3NH_2Ph$, m. p. 114°; $Al_2Br_6,4NH_2Ph$, m. p. 105°; $Al_2Br_6,8NH_2Ph$, m. p. 122°. These compounds dissolve in benzene or ether, and are decomposed by water, giving aluminium hydroxide and aniline hydrobromide.

p-Bromoaniline gives two compounds: $Al_2Br_6,2C_6H_4Br\cdot NH_2$, m. p. 140°, and $Al_2Br_6,5C_6H_4Br\cdot NH_2$, m. p. 125°. Diphenylamine gives the compound $Al_2Br_6,2NHPh_2$, m. p. somewhat above 200°; dimethylaniline, $Al_2Br_6,2NMe_2Ph$, m. p. 95°; methylaniline, $Al_2Br_6,2NHMePh$, m. p. 78°; nitrobenzene, $Al_2Br_6,2Ph\cdot NO_2$, m. p. 84°; pyridine, $Al_2Br_6,4C_5NH_5$, m. p. about 170° (decomp.); benzonitrile, the three compounds: $Al_2Br_6,2Ph\cdot CN$, m. p. 140—150°; $Al_2Br_6,3Ph\cdot CN$, m. p. about 140°, and $Al_2Br_6,4Ph\cdot CN$, m. p. about 150°.

Of the oxygenated compounds, acids, alcohols, aldehydes, and ketones form double compounds with aluminium bromide (compare Walker and Spencer, Trans., 1904, **85**, 1106). Further, esters of benzoic acid give compounds of the formula $Al_2Br_6,2Ph\cdot CO_2R$, that formed by methyl benzoate having m. p. 100°. Esters of fatty acids react energetically with aluminium bromide, hydrogen bromide being evolved.

The double compounds formed by aluminium bromide with organic nitrogen compounds are more stable than those containing organic oxygen compounds. The existence of complex compounds containing an odd number of molecules of an organic compound leads to the conclusion that the aluminium bromide present exists in the form of a doubled molecule, Al_2Br_6. T. H. P.

Preparation of Sodium Arylimides. Deutsche Gold- & Silber-Scheide-Anstalt (D.R.-P. 215339).—The replacement of an aminic hydrogen atom by sodium in aniline has been shown to occur only after prolonged heating at a high temperature.

It is now found that the reaction takes place much more readily in the presence of a catalytic agent, such as copper, nickel, cobalt, or any other heavy metal, its oxide, or salt.

Under these conditions, sodium reacts with aniline at 140°; the reaction also takes place with *o*-toluidine or methylaniline; the products are hygroscopic, fairly-stable substances, but are decomposed by water into sodium hydroxide and original base. F. M. G. M.

Preparation of Cerium Phenoxides. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 214782).—The compounds formed by the interaction of cerium salts with phenolic compounds have similar disinfectant properties to the bismuth phenoxides, but are less toxic and irritating than the phenols themselves.

Cerium phenoxide, prepared from cerium nitrate, phenol, and sodium hydroxide, is pale brown, odourless, and insoluble in water; it contains 31% cerium.

Cerium o-methoxyphenoxide analogously prepared is pink, insoluble in water, but soluble in alcohol, chloroform, or ether.

Cerium β-naphthoxide has similar properties, and contains 30% of cerium. F. M. G. M.

Behaviour of Phenyl Sulphide towards Hydrogen Peroxide. Oscar Hinsberg (*Ber.*, 1910, 43, 289—290).—When a solution of phenyl sulphide in glacial acetic acid is treated with the equivalent quantity

of hydrogen peroxide at the ordinary temperature, phenyl sulphoxide is formed (compare Abstr., 1908, i, 875). If, however, an excess (more than 2 gram-molecules) of hydrogen peroxide is used, and the mixture kept at the room temperature, crystals of phenylsulphone begin to form after a few days. The quantity of sulphone is increased by precipitation with water. Phenylsulphoxide could not be detected in the reaction mixture.

If acetone is used as the solvent (compare Smiles and Gazdar, Trans., 1908, 93, 1833) there is no action between phenyl sulphide and hydrogen peroxide at the ordinary temperature. Reaction only takes place after heating for an hour in a sealed tube at 80—100°, and even in the presence of excess of hydrogen peroxide, only phenyl sulphoxide is formed.

It is assumed that when glacial acetic acid is used as the solvent, it takes part in the reaction, owing to the formation of peracetic acid, $CH_3{\cdot}CO{\cdot}O{\cdot}OH$. T. S. P.

p-Tolyl Trisulphide. Bror Holmberg (*Ber.*, 1910, 43, 226—227). —The author has shown previously (Abstr., 1908, i, 308) that the mercaptans and thionyl chloride interact, with the formation of disulphide, trisulphide, water, and hydrogen chloride. He now finds that thionylaniline also reacts with mercaptans; with ethyl mercaptan, thioglycollic acid, and ethyl thioglycollate, the reaction is so violent that the reagents must be diluted with ether or carbon tetrachloride. It is, however, very difficult to isolate pure products from the reaction mixture.

When *p*-tolyl mercaptan is used, the trisulphide is readily isolated. The mixture of the mercaptan and thionylaniline was heated on the water-bath. After cooling and remaining for a few days, a solid separated, which had m. p. 81—82°, and proved to be *p*-tolyl trisulphide. It forms small plates, thin prisms, or needles, and is pale yellow. The crude solid was contaminated with a yellow oil, which was a mixture of aniline, *p*-tolyl disulphide, and aniline sulphate, the latter compound resulting from the hydrolysis of some of the thionylaniline by water formed in the reaction with the mercaptan:

$$4RSH + C_6H_5N{:}SO = R_2S_2 + R_2S_3 + H_2O + C_6H_5{\cdot}NH_2.$$

The following summary shows that the melting points of the thio-diacetic acids and of the *p*-tolyl sulphides show a regularity similar to that observed in many homologous series of carbon compounds. However, the member with an uneven number of sulphur atoms has a higher melting point than the next member with an even number.

$S(CH_2{\cdot}CO_2H)_2$	129°	p-$(C_6H_4Me)_2S$	57°
$S_2(CH_2{\cdot}CO_2H)_2$	109	p-$(C_6H_4Me)_2S_2$	46
$S_3(CH_2{\cdot}CO_2H)_2$	124	p-$(C_6H_4Me)_2S_3$	82
$S_4(CH_2{\cdot}CO_2H)_2$	113	p-$(C_6H_4Me)_2S_4$	75

T. S. P.

Phenanthrene Series. XXVI. Conversion of 9-Chloro-10-hydroxyphenanthrene into other Phenanthrene Derivatives. Julius Schmidt and Hermann Lumpp (*Ber.*, 1910, 43, 423—438).—9-Chloro-10-hydroxyphenanthrene (Abstr., 1909, i, 35) can be used for

the preparation of 3-nitrophenanthraquinone (*loc. cit.*), of 9 : 10-chloro-3-bromohydroxyphenanthrene, and other phenanthrene derivatives.

9(10)-*Chloro*-3-*bromo*-10(9)-*hydroxyphenanthrene*, $C_{14}H_8OClBr$, prepared by the action of a carbon disulphide solution of bromine on 9-chloro-10-hydroxyphenanthrene, forms colourless prisms, m. p. 142°, and dissolves in aqueous solutions of alkalis. Its *acetyl* derivative, $C_{16}H_{10}O_2ClBr$, has m. p. 158—159°, and the *benzoyl* derivative,

$$C_{21}H_{12}O_2ClBr,$$

which crystallises in yellow prisms, m. p. 179—180°.

When reduced with zinc dust and glacial acetic acid, the bromo-derivative yields 3-*bromo*-9(10)-*hydroxyphenanthrene*, $C_{14}H_9OBr$, which could not be crystallised on account of the readiness with which it dissolves in most solvents. Its *acetyl* derivative, $C_{16}H_{11}O_2Br$, crystallises in pale yellow prisms, m. p. 135°. The position of the bromine atom in the chlorobromohydroxyphenanthrene follows from the readiness with which it can be oxidised by chromic acid to 3-bromophenanthraquinone (Schmidt and Ladner, *Ber.*, 1905, **37**, 3571), which appears to exist in yellow and reddish-brown chromo-isomerides.

The *dioxime*, $C_{14}H_9O_2N_2Br$, prepared by Schmidt and Söll's method (Abstr., 1907, i, 630), forms green, crystalline aggregates, m. p. 212° (decomp.). The *monosemicarbazone*, $C_{15}H_{10}O_2N_3Br$, forms yellow crystals, m. p. 242° (decomp.), and the *monophenylhydrazone*,

$$C_{20}H_{13}ON_2Br_2,$$

has m. p. 177°.

The quinone can be reduced to the quinol by means of phenylhydrazine, but it is difficult to isolate the free dihydroxy-compound. Its acetyl derivative, 3-*bromo*-9 : 10-*diacetoxyphenanthrene*, $C_{18}H_{13}O_4Br$, crystallises in colourless needles, m. p. 177—178°.

3 : 9(10)-*Dihydroxyphenanthrene*, $C_{14}H_8(OH)_2$, formed when the 3-bromo-9(10)-hydroxy-compound is fused at 340° with potassium hydroxide, crystallises in colourless prisms, m. p. 175°. The yield is small.

Fuming nitric acid converts the bromophenanthraquinone into a *dinitro*-derivative, $C_{14}H_5O_6N_2Br_2$, which crystallises in pale yellow, slender needles, m. p. 298°. The *monoxime*, $C_{16}H_6O_6N_3Br$, forms green prisms, m. p. 196° (decomp.); the *semicarbazone*, $C_{15}H_8O_6N_5Br$, forms yellowish-brown prisms, m. p. 272°.

The dinitro-quinone condenses with an alcoholic solution of *o*-phenylenediamine hydrochloride, yielding 3-*bromodinitrophenanthraphenazine*, $C_{20}H_9O_4N_4Br$, as a reddish-white powder, and, when heated on the water-bath with concentrated aqueous ammonia, the quinone yields 3-*bromonitroaminophenanthraquinone*, $NO_2{\cdot}C_{14}H_5BrO_2{\cdot}NH_2$, as a dark brown substance, m. p. 280—282° (decomp.). The *diacetyl* derivative, $C_{18}H_{11}O_6N_2Br$, forms an ochre-yellow powder, m. p. 260° (decomp.).

Reduction of the 3-bromodinitrophenanthraquinone with tin and concentrated hydrochloric acid leads to the formation of 3-*chlorodiaminophenanthraquinol*, which can be readily oxidised by atmospheric oxygen to 3-*chlorodiaminophenanthraquinone*, $C_{14}H_5ClO_2(NH_2)_2$. The base can be diazotised readily, and the diazo-solution forms azo-dyes with phenols. The *dioxime*, $C_{14}H_{11}O_2N_4Cl$, forms a deep bluish-black powder, m. p. 264° (decomp.). When the diamino compound is diazo-

tised and the solution boiled, *3-chlorodihydroxyphenanthraquinone*, $C_{14}H_5ClO_2(OH)_2$, is obtained as a dark red powder, which is not a substantive dye. The *acetyl* derivative, $C_{18}H_{11}O_6Cl$, forms brownish-red crystals, m. p. 245°. J. J. S.

Preparation of Carbonateguaiacol-5-sulphonic Acid and its Salts. F. Hoffmann, La Roche & Co. (D.R.-P. 215050. Compare Abstr., 1909, i, 789).—The preparation of carbonatoguaiacol-5-sulphonic acid and its salts by the action of concentrated sulphuric acid on guaiacol carbonate has been described previously. The free acid forms colourless to dark red, hygroscopic crystals; its cold aqueous solution gives no colour with ferric chloride, but, on heating, carbon dioxide is evolved.

Potassium carbonatoguaiacol-5-sulphonate crystallises in needles, has a neutral reaction, gives no colour with ferric chloride, but by prolonged boiling of its aqueous solution is decomposed into potassium guaiacol-5-sulphonate with evolution of carbon dioxide.

F. M. G. M.

Hydroxyphenylalkylamines and Dihydroxyphenylalkylamines. Carl Mannich and W. Jacobsohn (*Ber.*, 1910, 43, 189—197. Compare Rosenmund, this vol., i, 106; Barger, Trans., 1909, 95, 1123, 2193).—Homologues of *p*-hydroxyphenylamine have been obtained by reducing aldoximes or ketoximes to bases of the type $OMe\cdot C_6H_4\cdot CH_2\cdot CHR\cdot NH_2$ or $C_6H_3(OMe)_2\cdot CH_2\cdot CHR\cdot NH_2$, and converting these by heating with hydriodic acid into the corresponding phenolic amines. The ketones selected were *p*-methoxybenzyl methyl ketone, 3 : 4-methylenedioxybenzyl methyl ketone, and 3 : 4-dimethoxybenzyl methyl ketone; the aldehydes were *p*-methoxyphenylacetaldehyde and 3 : 4-dimethoxyphenylacetaldehyde.

To obtain *p*-methoxybenzyl methyl ketone, b. p. 136—140°/12 mm., anethole was converted into the dibromide, and this into the bromohydrin, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CHMeBr$, which on heating with alcoholic potassium hydroxide gave anetholoxide; this, on heating at 220°, undergoes rearrangement to the ketone, $OMe\cdot C_6H_4\cdot CH_2\cdot COMe$. The oxime, on reduction with sodium amalgam in acetic acid solution, forms p-*methoxyphenyl*iso*propylamine*, $OMe\cdot C_6H_4\cdot CH_2\cdot CHMe\cdot NH_2$, a colourless, strongly alkaline oil, b. p. 158°/25 mm.; the *hydrochloride* forms large, colourless crystals, m. p. 210°.

p-*Hydroxyphenyl*iso*propylamine* crystallises in colourless rosettes, m. p. 125—126°; the *hydriodide* has m. p. 155°.

iso*Eugenol methyl ether bromohydrin*, $C_6H_3(OMe)_2\cdot CH(OH)\cdot CHMeBr$, has m. p. 78°. It yields the oxide already described by Fourneau and Tiffeneau (Abstr., 1905, i, 591), which readily undergoes rearrangement to 3 : 4-dimethoxybenzyl methyl ketone, b. p. 198°/20 mm.

3 : 4-*Dimethoxyphenyl*iso*propylamine* is an almost colourless oil, b. p. 166—168°/20 mm.; the *hydrochloride* has m. p. 144°. 3 : 4-*Dihydroxyphenyl*iso*propylamine*, $C_6H_3(OH)_2\cdot CH_2\cdot CHMe\cdot NH_2$, yields a *hydrochloride*, m. p. 190—192°.

3 : 4-*Methylenedioxyphenyl*isopropylamine is a colourless oil, m. p. 157°/22 mm.; the hydrochloride has m. p. 180—181°.

Homoanisaldehyde, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHO$, is conveniently prepared by oxidation of *p*-methoxystyrene with mercury oxide and iodine; the oxime forms prisms, m. p. 120° (compare Rosenmund, this vol., i, 106).

The *oxime* of homoveratraldehyde crystallises in prisms, m. p. 90—91°; the *oxime* of veratraldehyde has m. p. 82°. On reduction, the oxime yields 3 : 4-*dimethoxyphenylethylamine*, a faintly yellow-coloured oil, b. p. 188°/15 mm.; the *hydrochloride* has m. p. 154—155°.

3 : 4-*Dihydroxyphenylethylamine*, $C_6H_3(OH)_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, forms a crystalline hydrochloride, decomp. 220°; it shows a green coloration with ferric chloride. E. F. A.

Quinocarbonium Perchlorates (II) and the Solvent Action of Chlorinated Ethanes. Karl A. Hofmann, Heinz Kirmreuther, and A. Thal (*Ber.*, 1910, 43, 183—188. Compare this vol., i, 3).—The triphenylcarbinyl perchlorates crystallise so well that pure preparations are readily obtained from impure carbinols. In accordance with their intense colour, they are easily ionised, so that in solvents such as tetrachloroethane, which is unable to dissociate triphenylmethyl chloride, they still conduct the electric current.

Aurin perchlorate forms doubly refractive, four-sided prisms, which in direct light are orange-red with a light blue reflex. *p*-Trianisylcarbinol perchlorate (compare Gomberg and Cone, this vol., i, 55) crystallises in cinnabar-red, flat needles. It is relatively stable towards water.

Triphenylcarbinyl perchlorate dissolves with a reddish-yellow coloration in tetrachloroethane, and tri-*p*-anisylcarbinol perchlorate with an intense orange coloration. Both solutions conduct electricity, likewise those of the perchlorates in ethylene chloride.

The solubility of the perchlorates in a number of solvents has been compared by the intensity of the colour produced in the saturated solution. The solvents take the following order, the more highly coloured coming first: ethylene chloride, tetrachloroethane, chloroform, dichloroethylene, pentachloroethane, trichloroethylene, perchloroethylene, carbon tetrachloride. The last two or three solvents only become coloured when boiled with the perchlorate. Mercuric chloride dissolves in these solvents in precisely the same order, the solubility being greatest in ethylene chloride and almost nothing in carbon tetrachloride. This confirms the view that the perchlorates are of the nature of metallic salts.

The solvents dissolve sulphur in an altogether different order, ethylene chloride being the least, perchloroethylene the most, effective solvent. E. F. A.

Action of α-Bromonaphthalene and Magnesium on Certain Carbonyl Compounds. E. Schurakovsky (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1687—1694).—The interaction of α-bromonaphthalene, magnesium, and acetone yields the compound $MgBr{\cdot}O{\cdot}CMe_2{\cdot}C_{10}H_7$,

which is decomposed by water, giving α-naphthyldimethylcarbinol (compare Grignard, Abstr., 1901, i, 393). When heated with anhydrous oxalic acid, this alcohol yields β-naphthylpropylene (Grignard, *loc. cit.*), b. p. 251—251·5°/744 mm., D_4^{25} 1·0078, n^{25} 1·60684; the molecular refraction, calculated according to the Lorenz and Lorentz formula, is 57·554, which, as is often the case with naphthalene derivatives, differs considerably from the calculated value, 55·387.

p-*Tolyl-α-naphthylmethylcarbinol*, $C_6H_4Me\cdot CMe(C_{10}H_7)\cdot OH$, prepared from α-bromonaphthalene, magnesium, and tolyl methyl ketone, was obtained as a dark viscous, impure mass. When heated with anhydrous oxalic acid, this alcohol loses water, giving as-*α-naphthyl-p-tolylethylene*, $C_6H_4Me\cdot C(C_{10}H_7):CH_2$, which is a viscous, faintly yellow liquid, b. p. 224—226°/20 mm., $D_4^{21·5}$ 1·0693, and combines with 2Br per mol.

Anisyl-α-naphthylcarbinol, $OMe\cdot C_6H_4\cdot CH(C_{10}H_7)\cdot OH$, prepared from α-bromonaphthalene, magnesium, and anisaldehyde, crystallises in small needles or rhombic prisms, m. p. 87°.

α-Naphthylpropenylcarbinol, $CHMe:CH\cdot CH(C_{10}H_7)\cdot OH$, prepared by the interaction of α-bromonaphthalene, magnesium, and crotonaldehyde, is a faintly yellow, viscous liquid, b. p. 204—210°/22 mm.

T. H. P.

Preparation of Nitriles. E. Emmet Reid (*Amer. Chem. J.*, 1910, **43**, 162—181).—It was shown by Letts (Abstr., 1872, 1020) that nitriles can be prepared by the action of potassium thiocyanate on organic acids. Krüss (Abstr., 1884, 1314) found in the case of benzonitrile that a better yield could be obtained with lead thiocyanate than with the potassium salt, the reaction being represented by the equation:

$$2C_6H_5\cdot CO_2H + Pb(CNS)_2 = 2C_6H_5\cdot CN + PbS + H_2S + 2CO_2.$$

In attempting to prepare benzonitrile by Krüss' method, the yield obtained amounted to only 36% of the calculated, and it was observed that only a very small quantity of hydrogen sulphide was evolved. It was therefore considered likely that the hydrogen sulphide might have entered into the reaction and led to the formation of complex products. In order to avoid the formation of hydrogen sulphide, a mixture of lead benzoate and lead thiocyanate was heated, and it was found that, in these circumstances, a much better yield of benzonitrile was obtained. Experiments have been made to ascertain the effect of heating lead, sodium, zinc, and barium benzoates with potassium cyanate, lead cyanate, potassium thiocyanate, lead thiocyanate, barium thiocyanate, lead ferrocyanide, lead cyanide and sulphur, lead ferrocyanide and sulphur, zinc ferrocyanide and sulphur, potassium ferrocyanide and sulphur, and silver cyanide and sulphur. In each case a considerable quantity of benzonitrile was obtained. The results of these experiments are tabulated.

The best method of preparing benzonitrile in the laboratory is to distil a mixture of dry zinc benzoate and dry lead thiocyanate, a yield of 79—91% being thus obtained. A mixture of equivalent quantities of lead ferrocyanide and sulphur may be used instead of the thiocyanate

and, in this case, a yield of about 74% is produced. The formation of the benzonitrile takes place as follows:

$$Zn(CO_2\cdot C_6H_5)_2 + Pb(CNS)_2 = PbS + ZnS + 2CO_2 + 2C_6H_5\cdot CN.$$

On applying this method to other acids, it was found that the nitriles of the three aminobenzoic acids, *p* nitrobenzoic acid, salicylic acid, and phthalic acid, could not be obtained in this way, but that when lead *m*- or *p*-bromobenzoate was distilled with lead thiocyanate, a satisfactory yield of the bromobenzonitrile was produced in each case. E. G.

Action of Alcoholic Hydrogen Chloride on *m*-Methylnitrosoaminobenzoic Acid. Josef Houben and Walter Brassert (*Ber.*, 1910, 43, 206—212. Compare Abstr., 1909, i, 921).—*m*-Aminobenzoic acid in glacial acetic acid is treated with methyl sulphate. After one hour's heating and keeping for twelve hours, the crystals of *m*-aminobenzoic acid sulphate are removed, and the filtrate is treated with sodium nitrite at 0°, whereby m-*methylnitrosoaminobenzoic acid*, $NO\cdot NMe\cdot C_6H_4\cdot CO_2H$, m. p. 179—180° (bath previously at 160°), is obtained, which separates, slightly impure, from water in blood-red leaflets, and is converted after two weeks by alcoholic hydrogen chloride into *ethyl* m-*methylaminobenzoate hydrochloride*, m. p. 137° (corr.), which is converted into *ethyl* m-*methylnitrosoaminobenzoate*, m.p. 32°, by nitrous acid at 0°. After twenty-four hours, *m*-methylnitrosoaminobenzoic acid and alcoholic hydrogen chloride yield m-*methylaminobenzoic acid hydrochloride*, $CO_2H\cdot C_6H_4\cdot NHMe,HCl$, m. p. 244°, which is converted by *N*-sodium hydroxide into *m*-methylaminobenzoic acid, m. p. 127° (corr.). C. S.

New Drugs. V. Alfred Einhorn (*Annalen*, 1910, 371, 125—131. Compare Abstr., 1900, i, 439, 493; 1903, i, 257; 1908, i, 312).—Mainly a résumé of the work which led to the preparation of novocaine (ω-diethylaminoethyl *p*-aminobenzoate hydrochloride: compare Farbwerke vorm. Meister, Lucius and Brüning, Abstr., 1907, i, 923). As far as can be ascertained, all soluble aromatic esters, with the apparent exception of α-cocaine (compare Willstätter, Abstr., 1896, i, 707), are capable of producing local anæsthesia to a greater or less degree. Generally speaking, the anæsthetic action is destroyed by the introduction of a carboxyl or sulphoxyl group into the molecule; other substituents, such as halogen, hydroxyl, alkoxyl, nitro, amino, etc., either increase or diminish, but never destroy completely, the activity of an aromatic ester. W. H. G.

Diethylaminoethyl and Piperidinoethyl *p*-Aminobenzoates. Alfred Einhorn and Emil Uhlfelder (*Annalen*, 1910, 371, 131—142).—An account of the preparation of diethylaminoethyl *p*-aminobenzoate (novocaine), piperidinoethyl *p*-aminobenzoate, and some derivatives of these esters, much of which has appeared already (compare Farbwerke vorm. Meister, Lucius and Brüning, Abstr., 1907, i, 923; 1908, i, 638).

Diethylaminoethyl *p*-aminobenzoate crystallises with $2H_2O$ in small needles, m. p. 51°; the anhydrous substance crystallises in plates, m. p. 61°; the following derivatives have been prepared: *mercuri-*

chloride, needles, m. p. 139°; *hydriodide*, small needles, m. p. 121—122°; *mercuri-iodide*, $C_{13}H_{20}O_2N_2,HI,HgI_2$, small, white needles, m. p. 127°; *nitrate*, needles, m. p. 100—101°; *argentonitrate*, needles, m. p. 107°; *sulphate*, prisms, m. p. 170°; *chlorate*,

$$C_{13}H_{20}O_2N_2,HClO_3,$$

needles, m. p. 89°; *borate*, $C_{13}H_{20}O_2N_2,4B(OH)_3$, small needles, m. p. 159—160°; *trichloroacetate*, prisms, m. p. 89°; *thiocyanate*, prisms, m. p. 83°; *phthalate*, prisms, m. p. 119°; *ethochloride*,

$$NH_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_3Cl,H_2O,$$

prisms, sinters at 135°, and is completely molten at 180°; the anhydrous ethochloride has m. p. 198° (decomp.); *acetyl* derivative, a viscid oil, the *hydriodide* of which, $C_{15}H_{22}O_3N_2,HI$, crystallises in small rosettes, m. p. 146—147; the *hydrochloride* of the *benzoyl* derivative,

$$C_{20}H_{24}O_3N_2,HCl,$$

forms small needles, m. p. 189°; the p-*nitrobenzoyl* derivative crystallises in small needles, m. p. 129—130°, and when reduced yields the corresponding p-*aminobenzoyl* derivative, small needles, m. p. 124°, the *hydrochloride* of which, $C_{20}H_{25}O_3N_3,HCl$, crystallises in needles, m. p. 221°.

Piperidinoethyl p-*acetylaminobenzoate*, $C_{16}H_{22}O_3N_2$, crystallises in needles, m. p. 86—87°; the *hydrochloride* has m. p. 228°; the ester is converted by a hot alcoholic solution of hydrogen chloride into the *dihydrochloride* of piperidinoethyl *p*-aminobenzoate, m. p. 225°.

W. H. G.

Alkylaminoalkyl *p*-Aminobenzoates. Alfred Einhorn, Karl Fiedler, Carl Ladisch, and Emil Uhlfelder (*Annalen*, 1910, 371, 142—161).—The compounds described in this paper were prepared subsequently to novocaine, but not one of them is more suitable than this substance for the purpose of producing local anæsthesia. They are all obtained by the reduction of the corresponding *p*-nitrobenzoates, which are prepared by the action of *p*-nitrobenzoyl chloride on the requisite alkamine.

Dimethylaminoethyl p-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NMe_2,$$

prepared by heating dimethylaminoethyl alcohol with *p*-nitrobenzoyl chloride at 130°, crystallises in slender, matted needles, m. p. 58—59°; when reduced with tin and hydrochloric acid, it yields the corresponding *amino*-compound, $C_{11}H_{16}O_2N_2$, crystallising in large prisms, m. p. 121°, the *hydrochloride* of which, $C_{11}H_{16}O_2N_2,HCl$, forms small, slender needles, m. p. 185—186°.

*Di*iso*propylaminoethyl* p-*nitrobenzoate* is an oil; the *hydrochloride*, $C_{15}H_{22}O_4N_2,HCl$, crystallises in small needles, m. p. 136·5°; the corresponding *amino*-compound, $C_{15}H_{24}O_2N_2$, crystallises in slender needles, m. p. 48°, and forms a *hydrochloride*, crystallising in prisms, m. p. 195°.

*Di*iso*butylaminoethyl* p-*nitrobenzoate* is an oil; the *hydrochloride*, $C_{17}H_{26}O_4N_2,HCl$, forms slender, felted needles, m. p. 160—161°; the *amino*-compound, $C_{17}H_{28}O_2N_2$, small, slender needles, m. p. 84—85°, forms a *hydrochloride*, which crystallises in prisms, m. p. 195—196°.

*Di*iso*amylaminoethyl* p-*nitrobenzoate* is an oil; the *hydrochloride*,

$C_{19}H_{30}O_4N_2$,HCl, crystallises in small needles, m. p. 123—124°; the *amino*-compound, $C_{19}H_{32}O_2N_2$, leaflets, m. p. 44—45°, forms a *hydrochloride*, crystallising in needles, m. p. 154°.

Diethylaminomethylmethylethylcarbinol, $NEt_2{\cdot}CH_2{\cdot}CMeEt{\cdot}OH$, prepared by the action of diethylamine on the corresponding chloro-compound, is an oil, b. p. 71—73°/15·5 mm.; the p-*nitrobenzoate* is an oil, the *hydriodide* of which, $C_{16}H_{24}O_4N_2$,HI, forms pale yellow crystals, m. p. 167°; the p-*aminobenzoate* is a pale yellow oil, the *picrate* of which, $C_{22}H_{29}O_9N_5$, is a pale yellow, crystalline powder, m. p. 121°.

Piperidinomethylmethylethylcarbinol, $NC_5H_{10}{\cdot}CH_2{\cdot}CMeEt{\cdot}OH$, is a colourless oil, b. p. 101—104°/18 mm.; the p-*nitrobenzoate* is a viscid, yellowish-brown oil, the *hydriodide* of which, $C_{17}H_{24}O_4N_2$,HI, crystallises in yellow leaflets, m. p. 190°; the p-*aminobenzoate* is an oil, crystalline salts of which could not be obtained.

Diethylaminomethylethylcarbinol has b. p. 197—200° (compare Paal and Weidenkaff, Abstr., 1906, i, 236); the p-*nitrobenzoate* is an oil, the *hydriodide* of which, $C_{17}H_{26}O_4N_2$,HI, crystallises in yellow prisms, m. p. 154°; the *hydrochloride* of the oily p-*aminobenzoate*, $C_{17}H_{28}O_2N_2$,HCl, forms rhomboidal crystals, m. p. 166—167°.

*Tetraethyldiamino*isopropyl p-*nitrobenzoate*,

$$NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH(CH_2{\cdot}NEt_2)_2,$$

forms yellow crystals, m. p. 41°; the *dihydrochloride* crystallises in slender, felted needles, m. p. 198°; the p-*aminobenzoate*, $C_{18}H_{31}O_2N_3$, crystallises in colourless leaflets, m. p. 50°; the *dihydrochloride* forms faintly yellow, slender needles, m. p. 222°.

*Dipiperidino*isopropyl p-*nitrobenzoate*,

$$NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH(CH_2{\cdot}NC_5H_{10})_2,$$

is an oil; the *dihydriodide* crystallises in lemon-yellow, slender needles, m. p. 232°; the corresponding *amino*-compound, $C_{20}H_{31}O_2N_3$, forms colourless prisms, m. p. 137·5°, the *dihydrochloride* of which crystallises in slender needles, m. p. 261°.

The p-*nitrobenzoate* of α-diethylaminopropane-βγ-diol, $NEt_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_4{\cdot}NO_2$ or $NEt_2{\cdot}CH_2{\cdot}CH(CO_2{\cdot}C_6H_4{\cdot}NO_2){\cdot}CH_2{\cdot}OH$, is an oil; the *hydrochloride* is a microscopic, crystalline powder, m. p. 152°; the corresponding *amino*-ester is an oil; the *di*-p-*nitrobenzoate*, $C_{21}H_{23}O_8N_3$, forms small, yellow needles, m. p. 90—92°; the *di*-p-*aminobenzoate* has m. p. 132°; the *hydrochloride*, $C_{21}H_{27}O_4N_3$,HCl, is a crystalline powder, m. p. 185°. The p-*nitrobenzoate* of the corresponding piperidino-compound, $C_{15}H_{20}O_5N_2$, forms leaflets, m. p. 60—63°; the *hydrochloride* crystallises in white needles, m. p. 212°; the p-*aminobenzoate*, $C_{15}H_{22}O_3N_2$, crystallises in prisms, m. p. 91°; the *hydrochloride* forms white needles, m. p. 206°; the *di*-p-*nitrobenzoate*, $C_5NH_{10}{\cdot}CH_2{\cdot}CH(CO_2{\cdot}C_6H_4{\cdot}NO_2){\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_4{\cdot}NO_2$, crystallises in pale, yellow prisms, m. p. 108°; the *di*-p-*aminobenzoate* crystallises in prisms, m. p. 127°; the *hydrochloride*, $C_{22}H_{27}O_4N_3$,HCl, forms small needles, m. p. 210·5°. W. H. G.

Esters and Alkylamino-esters of 3 : 4-Diaminobenzoic Acid. Alfred Einhorn and Emil Uhlfelder (*Annalen*, 1910, 371, 162—179. Compare Einhorn, Abstr., 1908, i, 639).—The compounds

described in this paper were prepared with the object of obtaining derivatives of alkyl 3 : 4-diaminobenzoates yielding salts with a neutral reaction, which could consequently be employed as anæsthetics. The esters of 3 : 4-diaminobenzoic acid when boiled with organic acids yield esters of 2-alkylbenziminazole-5-carboxylic acid, and when treated with acetyl chloride yield the corresponding dichloroacetyl derivatives; the latter substances interact with secondary bases, for example, piperidine, yielding the dipiperidinoacetyl compounds.

Methyl 2-methylbenziminazole-5-carboxylate,

$$\begin{matrix} C(CO_2Me)\cdot CH:C-N \\ \| \quad\quad\quad | \\ CH-\!\!-\!\!-CH:C\cdot NH \end{matrix} \!\!>\!\! CMe$$

crystallises in needles, m. p. 172°; the *hydrochloride* forms small needles, m. p. 257°; the *ethyl* ester crystallises in needles, m. p. 180°. *Methyl 2-ethylbenziminazole-5-carboxylate*, $C_{11}H_{12}O_2N_2$, crystallises in needles, m. p. 141°; the *hydrochloride* has m. p. 252°. The *dibenzoyl* derivative of methyl 3 : 4-diaminobenzoate, $C_{22}H_{18}O_4N_2$, crystallises in small, white needles, m. p. 231°; the *dichloroacetyl* derivative,

$$CO_2Me\cdot C_6H_3(NH\cdot CO\cdot CH_2Cl)_2,$$

forms needles, m. p. 177°; the *dipiperidinoacetyl* derivative,

$$CO_2Me\cdot C_6H_3(NH\cdot CO\cdot CH_2\cdot NC_5H_{10}),$$

has m. p. 108°.

Ethyl 3-nitro-4-chloroacetylaminobenzoate, $C_{11}H_{11}O_5N_2Cl$, crystallises in small, yellow needles, m. p. 102°. *Ethyl 3-nitro-4-piperidinoacetylaminobenzoate* crystallises in yellow needles, m. p. 70—71°, and when reduced with tin and hydrochloric acid below 35° yields the corresponding *amino*-compound, $C_{16}H_{23}O_3N_3$, small needles, m. p. 103°, the *hydrochloride* of which crystallises in leaflets, m. p. 204°, whilst at a higher temperature it is converted into *ethyl 2-piperidinomethylbenziminazole-5-carboxylate*, $C_{16}H_{21}O_2N_3$, an oil, the *dihydrochloride* of which crystallises in needles, m. p. 227°. The following compounds are similarly prepared: *ethyl 3-nitro-4-diethylglycylaminobenzoate*,

$$NEt_2\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3(NO_2)\cdot CO_2Et,$$

yellow needles, m. p. 71°; *ethyl 3-amino-4-diethylglycylaminobenzoate*, small needles, m. p. 64°; *hydrochloride*, needles, m. p. 194°; *ethyl 2-diethylaminomethylbenziminazole-5-carboxylate*, $C_{15}H_{21}O_2N_3$, pointed needles, m. p. 67°; *hydrochloride*, small needles, m. p. 173°; *dihydrochloride*, m. p. 199°.

Chloroethyl 3 : 4-diaminobenzoate, $C_6H_3(NH_2)_2\cdot CO_2\cdot CH_2\cdot CH_2Cl$, is obtained by acting on a mixture of 3 : 4-diaminobenzoic acid and ethylene chlorohydrin with hydrogen chloride in the presence of a small quantity of concentrated sulphuric acid; it crystallises in needles, m. p. 80°, and, when heated with diethylamine under pressure at 100—120°, yields the corresponding *diethylaminoethyl* ester, an oil, the *hydrochloride* of which, $C_{13}H_{21}O_2N_3$,HCl, forms needles, m. p. 163°; the *picrate* crystallises in yellow needles, m. p. 189—190°. The diethylaminoethyl ester undergoes the following changes: (1) with glyoxal, it yields *diethylaminoethyl quinoxaline-6-carboxylate*, an oil, the *hydrochloride* of which, $C_{15}H_{21}O_2N_3$,HCl, crystallises in needles, m. p. 187°; (2) when treated with sodium nitrite and hydrochloric acid, it yields *diethylaminoethyl 3 : 4-aziminobenzoate hydrochloride*, $C_{13}H_{18}O_2N_3$,HCl, small needles, m. p. 150—151°; (3) it condenses

with *p*-dimethylaminobenzaldehyde, yielding a *substance*, which crystallises in yellow needles, m. p. 161°, and with benzaldehyde, yielding an oily *substance*, the *hydrochloride* of which crystallises in prisms, m. p. 190°.

Piperidinoethyl 3 : 4-*diaminobenzoate* crystallises in needles, m. p. 103°; when heated with glacial acetic acid, it yields *piperidinoethyl* 2-*methylbenziminazole*-5-*carboxylate*, $C_{16}H_{21}O_2N_3$, needles, m. p. 159—160°, the *hydrochloride* and *dihydrochloride* of which crystallise in needles, m. p. 162—163° and 262° respectively.

Diethylaminoethyl 3-*nitro*-4-*dimethylaminobenzoate*, prepared from 3-nitro-4-dimethylaminobenzoic acid and diethylaminoethanol, is an oil; the corresponding *amino*-compound, also an oil, forms a *hydrochloride*, $C_{15}H_{25}O_2N_3$,HCl, which crystallises in needles, m. p. 164°.

Methyl 3 : 4-*tetramethyldiaminobenzoate dihydriodide*, prepared by heating methyl 3-amino-4-dimethylaminobenzoate with methyl iodide and methyl alcohol under pressure at 100°, crystallises in needles, m. p. 109—110°; the *dihydrobromide*, $C_{12}H_{18}O_2N_2$,2HBr, crystallises in needles, m. p. 205°; the correspondiug *diethylaminoethyl* ester is an oil; the *hydrochloride*, $C_{17}H_{29}O_2N_3$, crystallises in small, white needles, m. p. 140—141°. W. H. G.

Isomerism of Anils (Schiff's Bases). Otto Anselmino (*Ber.*, 1910, 43, 462—463. Compare Manchot and Furlong, Abstr., 1909, i, 805; this vol., i, 33; Anselmino, Abstr., 1906, i, 13; 1907, i, 913; Knoevenagel and Schrötter, Abstr., 1905, i, 64).—Polemical. J. J. S.

Differences between Cinnamic Acid from Storax and Synthetical Cinnamic Acid. C. N. Riiber and V. Moritz Goldschmidt (*Ber.*, 1910, 43, 453—462. Compare E. Erlenmeyer, jun., Abstr., 1907, i, 318; 1909, i, 156, 647, 648).—Although cinnamic acid from storax differs so materially in habit from the synthetical acid, it is shown that the characteristic crystallographic constants are the same for the two acids. The chief differences are (*a*) the extremely thin plates in which the synthetical acid crystallises; (*b*) the absence of definite faces in the crystals of the synthetical acid; the plates as a rule have a crinkled edge.

As the synthetical acid when repeatedly crystallised approaches the habit of the storax acid, the conclusion is drawn that the former acid is identical with the storax acid, but contains a small amount of an impurity which is gradually removed by repeated crystallisation. The presence of this impurity retards to an enormous extent the development of the crystals in the direction normal to the face *b*{010}.

By careful fractionation of the ethyl ester of the synthetical acid, it has been found possible to isolate a fraction b. p. about 120°/0·2 mm., which when hydrolysed gives an acid containing about 9% Cl. This acid is probably an impure chlorocinnamic acid, and it is shown that when this impure acid or when small amounts of either *o*- or *p*-chlorocinnamic acids are added to the acid from storax, they alter its crystalline habit and transform it into the characteristic crystals of the synthetical acid. The synthetical acid is thus the same

acid as that from storax, but contains a small amount of a chloro-acid which completely alters its crystalline appearance.

Erlenmeyer's hetero-acid contains a larger proportion of the chloro-acid than does the synthetical acid.

Erlenmeyer states that specimens of benzaldehyde which are free from chlorine yield the synthetical acid. It is shown that small amounts (0·3%) of *o*-nitrocinnamic acid have the same effect on the crystalline habit of the storax acid as larger amounts of the chloro-acids.

Erlenmeyer's *α*- and *β*-cinnamic acids are regarded as dimorphous forms (compare Lehmann, *Zeitsch. Kryst. Min.*, 1885, **10**, 329).

J. J. S.

Transformations of *allo*-Cinnamic and *iso*Cinnamic Acids. Carl Liebermann and H. Trucksäss (*Ber.*, 1910, **43**, 411—414. Compare this vol., i, 36).—It is shown that when *allo*cinnamic or *iso*cinnamic acid of m. p. 58° is crystallised from carefully rectified light petroleum (b. p. 30—40°), crystals of the *iso*-acid, m. p. 42°, can usually be obtained if proper precautions are taken. The method consists in introducing a comparatively dilute solution of the acid into a glass tube by means of a suitable funnel, and then boiling the solution for some little time, so that the walls of the tube are thoroughly purified, and also that the solution may be concentrated. The tube is then sealed, and when placed in ice-cold water or in a freezing mixture, crystals of the acid m. p. 42° separate. These occasionally become transformed into the less fusible acids during transference from the tube. J. J. S.

Mechanism of the Transformation of α-Hydroxy-βγ-unsaturated Acids into the Isomeric γ-Keto-acids. Emil Erlenmeyer (*Festschrift Otto Wallach*, 1909, 404—413).—A discussion on the course of the intramolecular rearrangement of α-hydroxy-βγ-unsaturated acids into γ-ketones (compare Fittig, Abstr., 1897, i, 14; 1898, i, 196), based on the author's investigations (compare Abstr., 1898, i, 668; 1903, i, 32, 414; 1904, i, 500, 892, 1025). W. H. G.

[Preparation of Triphenylmethane Colouring Matters from Diortho-substituted Benzaldehydes.] Anilinfarben- & Extrakt-Fabriken vorm. J. R. Geigy (D.R.-P. 213502. Compare Abstr., 1908, i, 986).—It has been shown previously that the diortho-substituted benzaldehydes when employed in the production of triphenylmethane dyes yield colours of remarkable depth and fastness; it is now found that these properties are enhanced when the two ortho-substituents consist of different halogen atoms. The following new aldehydes are described:

2-*Chloro*-6-*bromobenzaldehyde*, prepared from 2-chloro-6-bromotoluene, forms colourless, spear-shaped crystals, m. p. 68°.

2-*Chloro*-4:6-*dibromo*-5-*aminobenzaldehyde*, m. p. 124°, a colourless, crystalline powder, is obtained by the bromination in aqueous suspension of 2-chloro-5-aminobenzaldehyde. 2:4:6-*Tribromo*-5-*aminobenzaldehyde*, m. p. 136—137°. 2-*Chloro*-4:6-*dibromo*-5-*hydroxybenzaldehyde* crystallises in dark yellow needles, and has m. p. 116°.

F. M. G. M.

p-Methoxysalicylaldehyde. Paul Friedländer (*Monatsh.*, 1909, 30, 879 — 881).—Since *p*-methoxysalicylaldehyde (*o*-hydroxyanisaldehyde), prepared by the action of sodium hydroxide on 4-methoxy-2-keto-1-indoxylbenzene (compare Friedländer and Schuloff, Abstr., 1908, i, 674), did not have the properties of the *o*-hydroxyanisaldehyde described by Tiemann and Parrisius (compare Abstr., 1881, 270), the compound has been prepared by the method employed by these investigators, also by the action of methyl sulphate on 2 : 4-dihydroxybenzaldehyde, and found to be identical with that derived from 4-methoxy-2-keto-1-indoxylbenzene. It is shown, further, that the substance obtained by Goulding and Pelly from *Chlorocodon Whiteii* (Proc., 1908, **24**, 62) is *o*-hydroxyanisaldehyde.

o-Hydroxyanisaldehyde has m. p. 41°; the oxime has m. p. 138°; the phenylhydrazone has m. p. 138°; the *aldazine*,

$$[OMe\cdot C_6H_3(OH)\cdot CH{:}N-]_2,$$

forms small, greenish-yellow crystals, m. p. 220°. W. H. G.

Orthovanillin [2-Hydroxy-3-methoxybenzaldehyde] and its Derivatives. Francis A. M. Noelting (*Bull. Soc. Ind. Mulhouse*, 1909, **79**, 401—430).—The compound described by Tiemann and Koppe as *β-m*-methoxysalicylaldehyde (compare Abstr., 1882, 54) is definitely shown to be 2-hydroxy-3-methoxybenzaldehyde, for, when treated with acetic anhydride, it yields 8-methoxycoumarin.

A large number of hydroxy- and methoxy-derivatives of benzaldazine and benzylideneaniline have been prepared with the object of ascertaining the effect of these groups on the colour of the substance. It is found that the para-derivatives of benzaldazine are the most highly-coloured, whilst the ortho-substitution products of benzylideneaniline are more intensely coloured than the corresponding para-isomerides; for example, vanillaldazine is golden-yellow, whilst 2-hydroxy-3-methoxybenzaldazine is lemon-yellow; 2-hydroxy-3-methoxy benzylideneaniline is orange, whilst the 4-hydroxy-isomeride is pale yellow. The ortho-, meta-, and para-hydroxy-derivatives of benzylideneaniline are lemon-yellow, white, and pale yellow respectively; the methyl ethers are all colourless, although the hydrochlorides are lemon-yellow; the methoxy-derivatives of the methyl ethers are not coloured, although the introduction of a methoxy-group into the hydroxy-derivatives increases the colour. Derivatives of benzylideneaniline containing a hydroxy- or methoxy-group are rendered more intensely coloured by the introduction of a hydroxy-group.

2-Hydroxy-3-methoxybenzaldehyde crystallises in pale yellow needles, m. p. 45·5°, b. p. 265—266°; it dyes wool an intense yellow, and silk a pale yellow; the m. p.'s of various mixtures of this compound with vanillin are recorded; the *sodium* salt, $C_8H_7O_3Na,H_2O$, crystallises in lemon-yellow plates; the *benzoate* crystallises in small, white needles, m. p. 74—75°; the *oxime* crystallises in white needles; the *phenylhydrazone*, $OMe\cdot C_6H_3(OH)\cdot CH{:}N\cdot NHPh$, forms colourless needles, m. p. 130—131°; the *phenylmethylhydrazone* forms colourless crystals, m. p. 62°. The *methyl ether*, $C_6H_3(OMe)_2\cdot CHO$, crystallises in white needles, m. p. 52—53°, and dissolves in concentrated sulphuric acid to a blood-red solution; the finely-divided substance produces

violent sneezing; the *oxime* has m. p. 98—99°; the *phenylhydrazone*, m. p. 138°, is white. The parent substance couples with diazo-compounds, forming compounds of the type $\begin{matrix} C(CHO):CH & -- & C\cdot N_2R \\ | & & || \\ C(OH):C(OMe) & \cdot & CH \end{matrix}$, and forms *condensation products* with the following bases, the colours of which only are given: *α*-naphthylamine, scarlet; *β*-naphthylamine, crimson; *p*-toluidine, orange; *p*-anisidine, yellowish-orange; *p*-phenetidine, yellowish-orange; *o*-chloroaniline, bright red; dichloroaniline, bright red; *p*-nitroaniline, orange-red; *m*-nitrotoluidine, orange-yellow; *p*-phenylenediamine, scarlet; benzidine, brick-red.

o-*Methoxybenzylideneaniline*, m. p. 44°, is white; the *meta*-isomeride is also white; 3 : 4-*dihydroxybenzylideneaniline*, m. p. 172°, is bright yellow, whilst the *dimethyl ether*, m. p. 81°, is white; 2-*hydroxy*-3-*methoxybenzylideneaniline*, m. p. 84—85°, is orange, whilst the *methyl ether*, m. p. 82·5°, is white; 4-*hydroxy*-3-*methoxybenzylideneaniline*, m. p. 152—153°, is pale yellow.

m-*Hydroxybenzaldazine*, m. p. 204—205°, is pale yellow; 2-*hydroxy*-3-*methoxybenzaldazine*, m. p. 198—199°, is lemon-yellow, whilst the *methyl ether*, m. p. 151°, is pale yellow.

Dimethylaniline condenses with 2-hydroxy-3-methoxybenzaldehyde and 2 : 3-dimethoxybenzaldehyde, yielding 4′ . 4″-*tetramethyldiamino*-2‴-*hydroxy*-3‴-*methoxytriphenylmethane*, m. p. 144°, and 4′ : 4″-*tetramethyldiamino*-2‴ : 3‴-*dimethoxytriphenylmethane*, m. p. 130—131°, respectively; the *hydrochlorides* are green and bluish-green respectively.

8-*Methoxycoumarin* forms inodorous, white crystals, m. p. 89°.

W. H. G.

Carbonyl Group in the Nascent State. Pavel Iw. Petrenko-Kritschenko (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1698—1703).—A reply to Stewart and Baly (compare Abstr., 1907, i, 220).

T. H. P.

Tetrabromo*cyclo*pentenedione. C. Loring Jackson and H. A. Flint (*Amer. Chem. J.*, 1910, **43**, 135).—Jackson and Russe (Abstr., 1906, i, 290) found that by the action of fuming nitric acid and bromine on tetrabromo-*o*-benzoquinone, two substances were produced, one, yellow, m. p. 142°, and the other, white, m. p. 144—146°. The present investigation was undertaken with a view to the further study of these compounds.

The white substance could not again be obtained, but oxalic acid was invariably produced.

The yellow compound has been found to be identical with Henle's tetrabromo*cyclo*pentene-1 : 3-dione (Abstr., 1907, i, 223), and is shown to have the constitution $CO<\begin{matrix} CBr_2\cdot & CO \\ | & | \\ CBr= & CBr \end{matrix}$. It is readily decomposed by boiling water or alcohol, but is remarkably stable towards acids or oxidising agents, and can be boiled for several hours with fuming nitric acid without undergoing visible change. When the compound is treated with solution of sodium carbonate for several days at the ordinary temperature, it is converted into dibromomaleic

acid and methylene dibromide. The action of sodium methoxide on the compound also results in the formation of dibromomaleic acid.

By the action of aniline on tetrabromo*cyclo*pentene-1 : 3-dione, there are produced *tribromoanilino*cyclo*pentenedione*, $NHPh{\cdot}C_5O_2Br_3$, m. p. 178°, which crystallises in yellow needles, and *hydroxyanilinoanil*-cyclo*pentenedione*, $NPh{:}C_5O_2(OH){\cdot}NHPh$, which forms a dark red, amorphous powder, and does not melt below 300°.

When tetrabromo*cyclo*pentenedione is reduced with sulphurous acid, *dibromodiketo*cyclo*pentene*, $C_5H_2O_2Br_2$, m. p. 151°, is obtained, which crystallises in pale yellow plates, and, on treatment with bromine, is reconverted into tetrabromo*cyclo*pentenedione. Phenylhydrazine reacts with dibromo*cyclo*pentenedione with formation of a brown, amorphous *substance*, which does not melt below 300°. When dibromo*cyclo*pentenedione is treated with aniline, *bromoanilino*cyclo-*pentenedione*, $NHPh{\cdot}C_5H_2O_2Br$, m. p. 121° (decomp.), is produced, which forms slender, yellow needles, and is converted by sodium carbonate solution into 1-*anilino*-Δ^1-cyclo*propen*-3-*one*, $NHPh{\cdot}C\begin{matrix}CO\\ \|\\ CH\end{matrix}$, m. p. 221° (decomp.), which crystallises in yellow needles.

By the action of methyl alcohol on tetrabromodiketo*cyclo*pentene, *tribromodiketomethoxy*cyclo*pentene*, $OMe{\cdot}C_5O_2Br_3$, m. p. 67°, is obtained, which forms white, slender needles. The corresponding *ethoxy*-compound, m. p. 110°, crystallises in small, white needles, and is converted by aniline into *hydroxydiketoanilino*cyclo*pentene*,

$$NHPh{\cdot}C_5H_2O_2{\cdot}OH,$$

m. p. 140° (decomp.), a red, amorphous substance, which yields an *acetyl* derivative, m. p. 150° (decomp.), as a pale brown, amorphous powder.

E. G.

Nitrosation of the Simplest Cyclic Ketones. Walther Borsche (*Festschrift Otto Wallach*, 1909, 301—312).—*cyclo*Hexanone is converted by amyl nitrite in the presence of a small quantity of acetyl chloride into 1 : 3-*dioximino*-2-cyclo*hexanone*,

$$CH_2\begin{matrix}CH_2{\cdot}C(N{\cdot}OH)\\ CH_2{\cdot}C(N{\cdot}OH)\end{matrix}CO,$$

which crystallises in glistening, yellow needles, m. p. above 200° (decomp.), and is decomposed by water, alcohol, and dilute acids; the corresponding triketone could not be isolated. The dioxime when treated with an alcoholic solution of sodium ethoxide and benzoyl chloride yields a *substance*, $C_{20}H_{22}O_5N_3$ (?), crystallising in colourless needles, m. p. 92—93°; benzoylation in the presence of pyridine leads to the formation of a *dibenzoate*, $CH_2\begin{matrix}CH_2{\cdot}C(OBz){:}N\\ CH_2{\cdot}C(OBz){:}N\end{matrix}CO$ (?), which crystallises in slender, yellow needles, m. p. 170—172° (decomp.), and when boiled with an aqueous solution of sodium hydroxide is probably decomposed, thus: $C_{20}H_{16}O_5N_2 + 4NaOH = CN{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN + Na_2CO_3 + 2Ph{\cdot}CO_2Na + 2H_2O$. An alcoholic solution of phenylhydrazine converts the dioxime into 1 : 2 : 3-*triketo*cyclo*hexanetriphenyl-hydrazone*, $C_{24}H_{24}N_6$, which crystallises in slender needles, m. p. 182—183°. The dioxime interacts with *o*-phenylenediamine, yielding

1-*oximino*-1 : 2 : 3 : 4-*tetrahydrophenazine*, $C_6H_4<\begin{matrix}N:C\cdot C(N\cdot OH)\cdot CH_2\\ N:C-CH_2-CH_2\end{matrix}$, small, glistening, brown crystals, m. p. 216—218°.

3·5-*Dioximino*-1-*methyl*-4-cyclo*hexanone*, $C_7H_{10}O_3N_2$, prepared from 4-methyl*cyclo*hexanone, crystallises in pale yellow leaflets, turns brown at 180°, and decomposes suddenly at 208°. The following derivatives are prepared by the methods just described: *dibenzoate*, small, pale yellow needles, decomposing at 172°; 3 : 4 : 5-*triketo*-1-*methyl*cyclo*hexanetriphenylhydrazone*, $C_{25}H_{20}N_6$, small, slender, yellow needles, m. p. 184°; 1-*oximino*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenazine*, $C_{13}H_{13}ON_3$, small, glistening, yellow needles, m. p. 210—211°. The parent substance is converted (1) by a cold solution of phenylhydrazine in glacial acetic acid into 3 : 5-*dioximino*-1-*methyl*cyclo*hexan*-4-*onephenylhydrazone*, $C_{13}H_{16}O_2N_4$, a crystalline, orange powder, m. p. 220° (decomp.); (2) an alcoholic solution of semicarbazide hydrochloride and sodium acetate into the *semicarbazone*, $C_8H_{13}O_3N_5$, which crystallises in spherical aggregates of small, colourless needles and decomposes at 200°; (3) by an alcoholic solution of hydroxylamine hydrochloride and sodium acetate into the corresponding *trioxime*, a colourless syrup, the *dibenzoate* (?) of which, $C_{21}H_{19}O_5N_3$, crystallises in small, colourless needles, m. p. 175°.

1 : 3-*Dioximino*-2-cyclo*pentanone*, $C_5H_6O_3N_2$, prepared from *cyclo*pentanone, crystallises in flat, yellow needles, and decomposes suddenly at 215°. W. H. G.

Catalytic Preparation of Aromatic Ketones. Jean B. Senderens (*Compt. rend.*, 1910, 150, 111—112. Compare Abstr., 1909, i, 286, 627; this vol., i, 11).—The following aromatic ketones are readily obtained by the method already described, namely: acetophenone, propiophenone, phenyl propyl ketone, phenyl *iso*propyl ketone, phenyl *iso*butyl ketone. To obtain a good yield, it is necessary to employ 3 mols. of the fatty acid to 1 mol. of benzoic acid, and to maintain the temperature of the catalyst at 380—460°. The product is always accompanied by smaller quantities of the symmetrical aliphatic ketone. Benzoic acid may be replaced by its anhydride. Benzophenone could not be obtained by this method. W. O. W.

Additive Compounds of Ketones and Quinones with Acids and Phenols. Kurt H. Meyer (*Ber.*, 1910, 43, 157—164. Compare Abstr., 1908, i, 731; 1909, i, 395).—Whereas acetophenone only forms colourless double salts with metallic chlorides, benzophenone in many cases yields light yellow compounds. A yellow *nitrate*, $C_{13}H_{10}O\cdot HNO_3$, has been isolated, whilst the faintly yellow-coloured solution of benzophenone in sulphuric acid undoubtedly contains a coloured sulphate. Benzophenone has, although to a much less extent, the same properties of halochromism as distyryl ketone. The coloured compounds of benzophenone could not be isolated, but those of fluorenone are more characteristic. Two series of double salts are formed, the one a deep violet, represented by the compound with aluminium bromide, and the other, orange in colour. The solution in

sulphuric acid apparently contains both forms, as the deep violet solution becomes orange-red on the gradual addition of water, and finally colourless when the fluorenone separates.

Fluorenone also combines with phenols, forming deeply-coloured products. With α-naphthol, two compounds are formed: an orange-yellow derivative from two molecules of fluorenone and one molecule of α-naphthol, and a red substance from one molecule of each component.

Similar compounds could not be obtained from distyryl ketone. Dianisylideneacetone, however, dissolves in phenol with an intense yellow coloration, and forms with α-naphthol a crystalline, orange-yellow compound, containing three molecules of α-naphthol to two molecules of the ketone.

These compounds of ketones and quinones with phenols are regarded as belonging to the same class of additive compounds as those with acids, metallic chlorides, and sulphur dioxide. Both classes possess a deep colour, pronounced crystallising power, and are easily resolved into their components by water, or when heated in solvents; their formation is exothermic. They are regarded as loose additive products to the quinonoid or ketone oxygen atom. *Fluorenone nitrate* forms orange-red needles; the *trichloroacetate* gives orange needles, m. p. 58°; the *mercurichloride*, $C_{13}H_8O,(HgCl_2)_2$, separates in lustrous, orange needles. The *stannichloride*, $(C_{13}H_8O)_2,SnCl_4$, forms brownish-yellow crystals. With sulphur dioxide a substance crystallising in orange needles is obtained, containing between 1 and $1\frac{1}{2}$ mols. of sulphur dioxide. *Fluorenone aluminium bromide* separates in dark red, almost black crystals. The *compound*, $2C_{13}H_8O,C_{10}H_8O$, produced on heating with α-naphthol, crystallises in long, orange needles, m. p. 66—67°. In presence of an excess of α-naphthol this is converted into $C_{13}H_8O,C_{10}H_8O$, separating in stout, red crystals, m. p. 89°.

The compound of 2 mols. of dianisylylideneacetone and 3 mols. of α-naphthol separates in long, orange needles, m. p. 69°. Dianisylylideneacetone and sulphur dioxide form an orange-yellow solution, giving rise to orange-yellow needles when concentrated.

Phenanthraquinone trichloroacetate, $C_{14}H_8O_2,C_2HO_2Cl_3$, crystallises in sealing-wax red needles, m. p. 138°. E. F. A.

Occurrence of β-Pinene and *l*-Pinocamphone in Hyssop Oil, and Some Observations on Isomerides in the Pinene Series. Eduard Gildemeister and Hugo Köhler (*Festschrift Otto Wallach*, 1909, 414—438).—An account of part of this investigation has appeared previously (compare Schimmel & Co., Abstr., 1908, i, 666). *l*-Pinocamphone, obtained directly from hyssop oil, has b. p. 212—213°/752 mm., D_{15}^{15} 0·9662, n_D^{20} 1·47421, α_D −13·7°, whilst a sample prepared by reducing the dibromide had b. p. 212·5—213·5°/749 mm., D_{15}^{15} 0·9679, n_D^{15} 1·47509, n_D^{20} 1·47343, α_D −19·33°; the dibromide has $[\alpha]_D^{21}$ −49·24° in ether; the *semicarbazone* has m. p. 228—229°; a small quantity of a second *semicarbazone*, m. p. about 182—183°, was also obtained; the *oxime* is a colourless oil, b. p. 105—110°/4 mm., which deposits well-defined crystals, m. p. about

37—38°, when kept for some time. The ketone is reduced by alcohol and sodium, yielding l-*pinocampheol*, long, matted needles, m. p. 67—68°, b. p. 217—218°, α_D −44·63°, $[\alpha]_D^{21}$ −55·33° in alcohol, D_{15}^{15} 0·9678, n_D^{15} 1·48420, n_D^{20} 1·48335 ; the corresponding *phenylurethane* crystallises in silky needles, m. p. 76—77°. *l*-Pinonic acid, obtained by the oxidation of the ketone, is identical with that described by Barbier and Grignard (compare Abstr., 1908, i, 852) ; when acted on by concentrated sulphuric acid, it yields l-*menthoethylheptanonolide*, crystallising in rectangular plates, m. p. 46—47°.

An attempt to prepare a pure active pinene by way of the crystalline *xanthate*, m. p. 36—37°, derived from *l*-pinocampheol (compare Tschugaeff, Abstr., 1908, i, 93), led to the production of a mixture of pinene and a dicyclic *terpene* ; the latter, when oxidised, gave a crystalline dicarboxylic *acid*, $C_{10}H_{16}O_4$, m. p. 192—193°.

W. H. G.

Constituents of Ethereal Oils. Tetrahydrosantalene, $C_{15}H_{28}$. Friedrich W. Semmler (*Ber.*, 1910, **43**, 445—448. Compare Abstr., 1907, i, 431, 433, 1062 ; 1908, i, 433).—*Santalene dihydrochloride*, $C_{15}H_{24}$,2HCl, obtained by the addition of hydrogen chloride to santalene in methyl-alcoholic solution, has b. p. 140—142°/0·55 mm., D^{20} 1·076, and n_D 1·4976. When distilled under 10 mm. pressure, it decomposes to a certain extent, yielding hydrogen chloride, and, when boiled with alcoholic potassium hydroxide, yields *β*-santalene.

When the dihydrochloride is reduced with sodium and boiling ethyl alcohol, it yields a mixture of hydrocarbons boiling at 119—123°/9 mm. The unsaturated hydrocarbons may be removed from this mixture by treatment with ozone, when pure *tetrahydrosantalene*, $C_{15}H_{28}$, is obtained. It has b. p. 116—118°/9 mm., D^{20} 0·864, n_D 1·4676, and α_D +7°30′ (100 mm. tube). The hydrocarbon must be dicyclic, as it has all the properties of a saturated compound ; it is thus analogous to dihydroeksantalol and dihydroeksantalic acid. J. J. S.

Action of Magnesium and Allyl Bromide on Menthone. P. Ryschenko (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1695—1698 Compare Javorsky, Abstr., 1909, i, 168).—1-*Methyl*-4-iso*propyl*-3-*allyl*-cyclo*hexan*-3-*ol*, $CH_2<\begin{matrix}CHMe-CH_2\\CH_2\cdot CHPr^{\beta}\end{matrix}>C(CH_2\cdot CH{:}CH_2)\cdot OH$, obtained on decomposing by means of water the Grignard compound yielded by magnesium, allyl bromide, and menthone, is a mobile, colourless liquid, b. p. 130—131°/22 mm., D_4^{27} 0·9028, *n* 1·470035, with an odour like that of mint. On oxidation with permanganate, it yields (1) menthol-acetic acid, $CH_2<\begin{matrix}CHMe-CH_2\\CH_2\cdot CHPr^{\beta}\end{matrix}>C(CH_2\cdot CO_2H)\cdot OH$, which, when heated with potassium hydrogen sulphate, loses water and gives an acid, $C_{12}H_{20}O_2$; both of these acids were obtained by Wallach (Abstr., 1902, i, 799) ; (2) the *trihydric alcohol*,

$$CH_2<\begin{matrix}CHMe-CH_2\\CH_2\cdot CHPr^{\beta}\end{matrix}>C(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

which is a pale yellow, syrupy, odourless liquid. T. H. P.

Behaviour of Alicyclic Hydroxylamines and Hydroxylamineoximes towards Nitrous Acid. I. Guido Cusmano (*Gazzetta*, 1909, 39, ii, 453—467. Compare Francesconi and Cusmano, Abstr., 1909, i, 723, 724).—*iso*Nitroamines form two classes of ethers: (1) NO·NR·OR′, which readily give up nitrous acid, and (2) $R\cdot N{:}N\cdot OR$ ($\overset{\|}{O}$) or $R\cdot N{-}N\cdot OR$ ($\diagdown O \diagup$), which, under similar conditions, are either stable or else yield nitrous oxide. Analogous behaviour is shown by the two classes of ether formed by the nitroamines, namely, (1) $NO_2\cdot NRR'$, which decompose, giving nitrous acid, and

(2) $R\cdot N{:}N\cdot OR'$ ($\overset{\|}{O}$) or $R\cdot N{-}N\cdot OR'$ ($\diagdown O \diagup$),

which yield nitrous oxide. It seems, then, that in these ethers the complex $-N_2O_2-$ can be completely eliminated from the forms $-N{:}N\cdot O-$ ($\overset{\|}{O}$), $N{:}N\cdot O\cdot$ ($\overset{\|}{O}$), and $\cdot N{-}N\cdot O\cdot$ ($\diagdown O \diagup$), but not from the forms $-N(NO_2)-$ and $-N(NO)\cdot O-$. Hence the nitroamines and *iso*nitroamines, which in the free state probably possess the forms $R\cdot NH\cdot NO_2$ and $R\cdot N(OH)\cdot NO$ respectively, retain these forms when they decompose with elimination of nitrous acid, but assume the forms $R\cdot N{:}NO\cdot OH$ and $R\cdot NO{:}N\cdot OH$ when decomposition is accompanied by separation of hyponitrous acid or nitrous oxide and water. As a rule, the known *iso*nitroamines exhibit one or other of the above two methods of decomposition, but the author finds that, by varying the conditions, pulegonenitrosohydroxylamine (menth*oiso*nitroamine) can be decomposed in both ways, and can hence react in the two forms:

$$CHMe\langle{}^{CH_2\cdot CH_2}_{CH_2-CO}\rangle CH\cdot CMe_2\cdot N(NO)\cdot OH \text{ and}$$

$$CHMe\langle{}^{CH_2\cdot CH_2}_{CH_2-CO}\rangle CH\cdot CMe_2\cdot NO{:}N\cdot OH.$$

By the action of hydroxylamine on pulegone, three compounds have been obtained: pulegonehydroxylamine, m. p. 154° (compare Beckmann and Pleissner, Abstr., 1891, 936), an oxime, m. p. 120° (compare Wallach, Abstr., 1896, i, 309), and [α] pulegonehydroxylamineoxime, m. p. 118° (compare Semmler, Abstr., 1905, i, 222). The author has obtained two new derivatives of pulegone, namely, an oxime, m. p. 98°, and a [β] hydroxylamineoxime, m. p. 143°. Wallach (Terpene und Campher, Leipzig, 1909) regards the oxime m. p. 120° as an oxime of *iso*pulegone, and the oxime m. p. 98° is either stereoisomeric with this,

$$CHMe\langle{}^{CH_2\cdot CH_2}_{CH_2-C(N\cdot OH)}\rangle C{:}CMe_2 \text{ and } CHMe\langle{}^{CH_2\cdot CH}_{CH_2-C(OH\cdot N)}\rangle C{:}CMe_2,$$

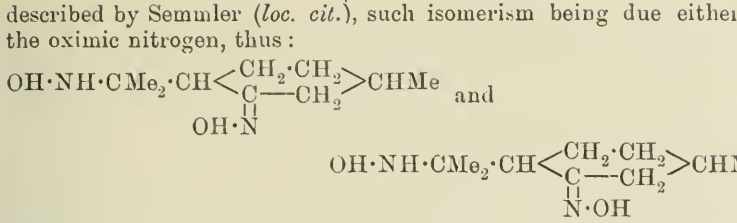
or structurally isomeric,

$$CHMe\langle{}^{CH_2-CH_2}_{CH_2\cdot C(NOH)}\rangle CH\cdot CMe{:}CH_2 \text{ and}$$

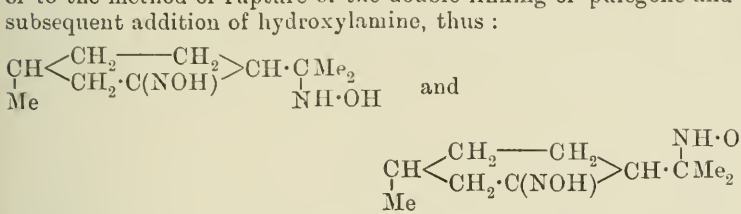
$$CHMe\langle{}^{CH_2-CH_2}_{CH_2\cdot C(NOH)}\rangle C{:}CMe_2.$$

The new hydroxylamineoxime, m. p. 143°, is stereoisomeric with that

described by Semmler (*loc. cit.*), such isomerism being due either to the oximic nitrogen, thus :



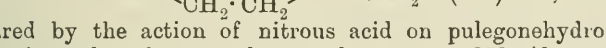
or to the method of rupture of the double linking of pulegone and the subsequent addition of hydroxylamine, thus :



Pulegoneoxime, $C_{10}H_{16}{:}NOH$, m. p. 98°, prepared by the action of hydrochloric acid on *iso*pulegoneoxime, m. p. 120°, forms groups of laminæ with triangular sections, reduces Fehling's solution, and is rapidly decomposed by heating with dilute sulphuric acid, but is not affected by boiling with alcoholic potassium hydroxide.

β-Pulegonehydroxylamineoxime, $C_{10}H_{20}O_2N_2$, which is obtained together with the α-isomeride and *iso*pulegoneoxime when pulegone and hydroxylamine react under certain conditions, forms shining needles, m. p. 143°, reduces Fehling's solution instantaneously in the cold, and, when dissolved in organic solvents, is oxidised by the air to nitroso-compounds of a blue colour.

Pulegonenitrosohydroxylamine,



prepared by the action of nitrous acid on pulegonehydroxylamine, forms irregular, hexagonal crystals, m. p. 35° (decomp.), gives Liebermann's and the diphenylamine reactions, and in ethereal or alcoholic solution gives a garnet-red coloration with ferric chloride ; it does not reduce Fehling's solution, but forms a *semicarbazone*, $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}C_{10}H_{17}{\cdot}N(NO){\cdot}OH$, m. p. 165° (decomp.), which gives Liebermann's and the diphenylamine reactions and a red coloration with ferric chloride. With hydroxylamine in alcoholic solution, pulegonenitrosohydroxylamine gives a white, hygroscopic *substance*, decomp. at 200°, which reduces Fehling's solution in the cold and gives Liebermann's reaction, but gives no coloration with ferric chloride. When suspended in water or dissolved in organic solvents, pulegonenitrosohydroxylamine is moderately stable, but in the dry state in the air, or in a vacuum, it undergoes rapid decomposition, yielding (1) pulegone and (2) 8-nitromenthone (compare Harries and Roeder, Abstr., 1900, i, 182), which results from the oxidation of the 8-nitrosomenthone formed initially by the action of the air and of the nitric acid eliminated. With nitrous acid, pulegonenitrosohydroxylamine gives

pulegone and nitro- and nitroso-menthones. The last two compounds are formed according to the equation :

$$C_{10}H_{17}O\cdot NH\cdot OH + C_{10}H_{17}O\cdot N(NO)\cdot OH + HNO_2 = C_{10}H_{17}O\cdot NO_2 + C_{10}H_{17}O\cdot N_2O + N_2 + 2H_2O.$$

The formation of pulegone by the action of nitrous acid is due to the diazotisation of the pulegonenitrosohydroxylamine, thus :

$$C_{10}H_{17}O\cdot N(NO)\cdot OH + HNO_2 = C_{10}H_{17}O\cdot N_2\cdot NO_3 + H_2O ;$$

the resulting aliphatic diazo-derivative is immediately decomposed by water into nitrogen, nitric acid, and 8-hydroxymenthone, the last compound then losing water and giving pulegone. When, however, decomposition of pulegonenitrosohydroxylamine occurs in presence of an alkali, it proceeds entirely in the one direction, the resultant products being pulegone and nitrous oxide: $C_{10}H_{17}O\cdot NO{:}N\cdot OH + H_2O = C_{10}H_{17}O\cdot OH + H_2O + N_2O$ and $C_{10}H_{17}O\cdot OH = C_{10}H_{16}O + H_2O$.

T. H. P.

New Occurrence of *l*-Camphor. Theodor Whittelsey (*Festschrift Otto Wallach*, 1909, 668—670).—The oil obtained from a variety of "sage-brush" common to western North America, probably *Artemisia cana*, was found to have the following constants: D_{15}^{15} 0·9405 ; α_D^{19} −19·09° ; $n_D^{20\cdot5}$ 1·4702 ; acid number, 4·2, 4·1 ; ester number, 18·5, 19·8 ; saponification number, 22·7, 23·9 ; saponification number after acetylation, 111·8, 110·3. It contains *l*-camphor to the extent of at least 44·5%, an observation not without interest, for, with the exception observed by Wallach in the case of the broad-leafed *Salvia*, *l*-camphor has been found only in plants of the family *Compositae*.

W. H. G.

Coriander Oil. Heinrich Walbaum and Wilhelm Müller (*Festschrift Otto Wallach*, 1909, 654—667).—The sample of coriander oil examined had the following constants: D_{15}^{15} 0·8735 ; α_D +10·4° ; n_D^{20} 1·46387 ; acid number, 0 ; ester number, 20·22 ; ester number after acetylation, 159, corresponding with 49·65% of linalool ; it is possible to obtain, however, 70% of the latter substance by fractional distillation on a large scale. Roughly, 20% of the oil consists of almost equal quantities of *α-d*-pinene, *p*-cymene, and terpinenes (*α*- and *γ*-terpinene), together with very small quantities of *β*-pinene, dipentene, and possibly, also, phellandrene and terpinolene. The presence of decylaldehyde, geraniol, *l*-borneol, and esters of these alcohols was also established. In addition to the compounds mentioned, coriander oil contains small quantities of unknown substances, which are of importance in imparting aroma to the oil.

W. H. G.

[Essential Oils.] Roure-Bertrand Fils (*Sci. Ind. Bull. Roure-Bertrand Fils*, 1909, [ii], 10, 19—43).—This contains the following new work :

[Justin Dupont and Louis Labaune.]—*Action of Hydrochloric Acid on Linalool and Geraniol* (compare Grosser, Abstr., 1882, 525 ; Barbier, *ibid.*, 1892, 1236 ; 1895, i, 78).—When dissolved in toluene and treated with gaseous hydrogen chloride at 100°, both alcohols yield *linalyl chloride*, $C_{10}H_{17}Cl$, D^{20} 0·9341, $[\alpha]_D^{20}$ 1·50°, n_D^{20} 1·4813, and b. p. 95—96°/6 mm. This on treatment with silver nitrate in alcohol

regenerates linalool. The chloride obtained from geraniol could not be obtained quite pure. At $-4°$ to $+3°$ the action of hydrogen chloride on linalool or geraniol in toluene is more complicated. No water is formed until the mixture regains atmospheric temperature. The product formed is a mixture of linalyl chloride with a dichloro-derivative. Cinnamyl alcohol at 100° yields a *chloride*, C_9H_9Cl, D^{22} 1·0857, n_D^{22} 1·583, b. p. 115—116°/6 mm., which absorbs bromine, forming a *dibromide*, m. p. 104°, and on treatment with silver nitrate in alcohol yields a mixture of two alcohols, one of which may be phenylallyl alcohol (Klages and Klenk, Abstr., 1906, i, 638).

[J. Leroide.]—*Preparation of Fenchone free from Camphor.*—The best results were obtained by warming crude fenchone with aluminium chloride and then distilling under reduced pressure. For the detection of camphor the semicarbazide test was employed, which is sufficient to show the presence of 0·1% of camphor. By this means camphor was proved to occur naturally in fennel oil. Thujone cannot be eliminated from mixtures of this ketone with camphor and fenchone by treatment with aluminium chloride and bromine, and in such cases oxidation with nitric acid must be resorted to, the camphor being subsequently removed by treatment with aluminium chloride and bromine.

Four oils from the Comores Islands were examined, and gave the following results: Bigarade oil had D^{15} 0·8812, α_D +42°13′, and was insoluble in 80% alcohol.

Petitgrain oil had D^{15} 0·8650, α_D +42°18′, and saponification value 33·6.

Basil oil had D^{15} 0·9588, α_D 0°35′, and saponification value 4·2.

Citronella oil had D^{15} 0·8922, α_D −0°52′, aldehydes 80% (by bisulphite process), and was insoluble even in absolute alcohol.

Ylang-ylang oil, from Nossi-Bé, had D^{15} 0·9673, α_D −42°12′, acid value 1·4, saponification value 129·5, esters 45·3%, and total alcohols 42·7%.

Linaloe oil, from Cayenne, had D^{20} 0·8721, α_D −12°56′, n_D^{20} 1·4635, and contained methylheptenone, *d*-terpineol, geraniol, *l*-linalool, and nerol (?). T. A. H

Constituents of Oil of Lemon. Eduard Gildemeister and Wilhelm Müller (*Festschrift Otto Wallach*, 1909, 439—451).—Oil of lemon contains in addition to *l*-limonene a moderate quantity of *l*-β-pinene, and very small quantities of α-pinene, *i*-α-pinene, *l*-camphene, β-phellandrene, and γ-terpinene. The sesquiterpene obtained from the oil in small quantity (compare Burgess and Page, Trans., 1904, 85, 414) is shown to be identical with bisabolene (compare Tucholka, Abstr., 1897, ii, 584); the same hydrocarbon is present in opoponax oil, oil of *Piper Volkensii* (compare Schmidt and Weilinger, Abstr., 1906, i, 299), and camphor oil.

The erythritol from γ-terpinene (compare Wallach, Abstr., 1908, i, 814) undergoes the following changes: (1) when boiled with acids it yields a mixture of thymol and carvacrol; (2) it yields a brominated *substance*, crystallising in large leaflets, m. p. 93—94°, when treated with an alkaline solution of hypobromite; (3) when oxidised with an

alkaline solution of potassium permanganate it yields oxalic acid and an acid, m. p. 147—149°, which is probably *iso*propyltartronic acid.

W. H. G.

Essential Oil from the Seeds of Monodora grandiflora. Robert Leimbach (*Festschrift Otto Wallach*, 1909, 502—512).—The oil obtained by the steam distillation of the seeds of *Monodora grandiflora* is a limpid, pale yellow oil, with an odour resembling cymene, D_{15}^{15} 0·8574, α_D^{15} −46·25° in a 1-dcm. tube, acid number 3·9, saponification number 7—12. Nearly 90% of the oil consists of hydrocarbons, chiefly *l*-phellandrene, camphene, and *p*-cymene. The remainder, a heavy oil with an aromatic odour, contains palmitic acid, carvacrol, a *substance*, $C_{10}H_{16}O$, which reacts neither as an alcohol nor a ketone, a *sesquiterpene*, $C_{15}H_{24}$, b. p. 260—270°, D_{15}^{15} 0·9138, α_D +24°, n_D^{16} 1·50513, a crystalline *substance*, m. p. 160—163°, and small quantities of other unknown substances. W. H. G.

A Condensation Product of Coumaranone and its Conversion into Oxindirubin. Karl Fries and W. Pfaffendorff (*Ber.*, 1910, 43, 212—219).—The constitutions have been ascertained of the compound, $C_{18}H_{14}O_4$, obtained from 4-methyl-2-coumaranone or from ω-chloro-2-hydroxy-5-methylacetophenone (Abstr., 1909, i, 44), and also of those obtained by a similar process from 5-methyl-2-coumaranone or ω-chloro-2-hydroxy-4-methylacetophenone, and from 2-coumaranone or ω-chloro-2-hydroxyacetophenone. An ethereal solution of 2-coumaranone is treated with sodium and then with acetyl chloride, whereby the *acetate*, m. p. 106°, of 2-hydroxy-1 : 2′-dicoumarone, $C_6H_4<^{C(OH)}_{O}>C\cdot C<^{C_6H_4}_{CH\cdot O}$, is formed; the parent substance has not been obtained pure. By warming an alcoholic solution of the acetate with sodium ethoxide and subsequently acidifying, by boiling an acetic acid solution of the acetate with hydrogen peroxide, or by the prolonged heating of 2-coumaranone or ω-chloro-2-hydroxyacetophenone with alcoholic sodium ethoxide, 2 : 1′-*dihydroxy*-1 : 2′-*dicoumarone* (leuco-oxindirubin), $C_6H_4<^{C(OH)}_{O}>C\cdot C<^{C_6H_4}_{C(OH)\cdot O}$, m. p. 185°, is obtained, which forms orange-yellow needles, gives a deep red, non-fluorescent solution in concentrated sulphuric acid, and by the prolonged heating of its solution in glacial acetic acid, or, more readily, by treating the solution with hydrogen peroxide or bromine, is converted into "1 : 2-*biscoumaran-indigo*" (*oxindirubin*),

$$C_6H_4<^{CO}_{O}>C:C<^{C_6H_4}_{CO\cdot O},$$

m. p. 215°, which is also obtained by treating an acetic acid solution of 2-coumaranone and *o*-hydroxybenzoyl formic acid with concentrated sulphuric acid.

By a similar series of reactions, 5-methyl-2-coumaranone yields the *acetate*, m. p. 133°, of 2-hydroxy-5 : 5′-dimethyl-1 : 2′-dicoumarone, 2 : 1′-*dihydroxy*-5 : 5′-*dimethyl*-1 : 2′-*dicoumarone* (5 : 5′-*dimethyl-leuco-oxindirubin*), m. p. 204°, and "1 : 2′-*bis*(5-*methylcoumaran*)-*indigo*"

(5 : 5′-*dimethyloxindirubin*). The compound $C_{18}H_{14}O_4$ (*loc. cit.*) is 4 : 4′-dimethyl-leuco-oxindirubin. C. S.

Oxonium Perchlorates. Karl A. Hofmann, A. Metzler, and H. Lecher (*Ber.*, 1910, 43, 178—183. Compare Abstr., 1909, ii, 568).—Seventy per cent. perchloric acid yields crystalline compounds with ketones, and similar substances with basic properties; these are sparingly soluble and admirably adapted for characterising and isolating ketones. Even substances, such as carbazole, in which the basic properties of the nitrogen are very feeble, form crystalline salts. The perchlorates afford a better test of basic properties than picrates. These salts are regarded as oxonium derivatives.

A solution of xanthone in tetrachloroethane gives a bright yellow precipitate of *xanthone perchlorate*, $C_{13}H_8O_2,HClO_4$, which can be recrystallised from tetrachloroethane without decomposition, but is very rapidly decomposed by traces of moisture.

Carbazole perchlorate crystallises in lustrous, colourless plates; it is decomposed by water. Prolonged action with an excess of perchloric acid leads to the formation of a greenish-blue compound.

A colourless perchlorate is also formed by quinone di-imide. This explodes on heating. When moistened with water, it becomes a brilliant bluish-green, then violet, and then brown.

Benzophenone forms a yellow solution and a bright brownish-yellow, crystalline mass. This rapidly decomposes in moist air, leaving colourless oily drops, which do not crystallise until inoculated with a crystal of benzophenone. The perchlorate is apparently derived from the allotropic low melting variety of benzophenone.

Anthraquinone and alizarin do not react with perchloric acid. *Phenanthraquinone perchlorate* forms a mass of blood-red crystals in solution, which dry to red needles, but rapidly become bright orange when exposed to moist air. The *hemiperchlorate*, $(C_{14}H_8O_2)_2,HClO_4$, is obtained in flat, obliquely-cut, yellow or brownish-red prisms.

From retenequinone only the *hemiperchlorate* has been isolated. *Naphthazarin perchlorate* forms large, rectangular, stout plates with a bronze lustre. E. F. A.

New Selenium Compound. Ida Foa (*Gazzetta*, 1909, 39, ii, 527—534).—*Selenophen*, $\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}\!\!>\!Se$, obtained by heating sodium succinate with phosphorus triselenide, is a yellow, mobile, irritant liquid, b. p. 147—149°/250 mm.; it dissolves in concentrated sulphuric acid, giving a reddish-brown coloration, whilst with a solution of isatin in concentrated sulphuric acid, a dark carmine coloration is obtained. In presence of acetic acid, it forms with bromine an unstable, liquid bromide. T. H. P.

Production of a Volatile Aromatic Substance from Solutions of Morphine Salts. C. Reichard (*Pharm. Zentr.-h.*, 1910, 51, 128—130).—When a solution of morphine hydrochloride or sulphate in water is heated, a slight odour of musk is developed, and the

strength of this odour increases with the concentration of the alkaloidal solution, and with the quantity of water vapour produced from the solution. T. A. H.

Partial Racemism. H. Dutilh (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 393—400).—The author has studied the partial racemism which occurs with strychnine racemate, more especially by observing the behaviour of this compound in presence of its aqueous solution. The investigation was carried out on the lines indicated by Roozeboom (Abstr., 1899, ii, 401), who pointed out the probable inaccuracy of the results obtained by Ladenburg and Doctor (Abstr., 1899, i, 310). By means of the solubility curves of the *d*-, *l*-, *l*+*r*-, and *d*+*r*-compounds at 40°, 25°, 16°, and 7·5°, it was found that the transition interval, which Ladenburg and Doctor assumed to be non-existent, extended over about 20°. Saturated solutions of the partial racemate are stable only below 7·5°, although the solubility at higher temperatures can be determined by retarding the decomposition.

The author has avoided determining by means of the polarimeter the content of the *l*- and *d*-compounds in liquids saturated with the *r*+*d*-, *r*+*l*-, or *d*+*l*-compounds, and suggests that such method of analysis gives a wrong idea concerning the inner composition of a solution saturated with two salts. This view is supported by the results obtained by Findlay and Hickmans (Trans., 1909, **95**, 1386), who, using the polarimetric method of estimation, found that the addition of *l*-menthyl *l*-mandelate diminishes the solubility of *l*-menthyl *d*-mandelate at 10°, whilst it increases it at 25° or 35°; such behaviour the author regards as improbable. T. H. P.

Hæmopyrrole. Leon Marchlewski (*Ber.*, 1910, **43**, 259—260).—Polemical. A reply to Piloty (this vol., i, 133). R. V. S.

Pyridine Hydrate. William Oechsner de Coninck (*Bull. Soc. chim. Belg.*, 1910, **24**, 55).—From basic tar oils the author has isolated a product which has the composition of a pyridine hydrate,

$$2C_5H_5N,7H_2O.$$

This has b. p. 91—93°, but it is not regarded as a definite chemical compound (compare Goldschmidt and Constam, Abstr., 1884, 611). T. A. H.

Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines. VI. Tautomerism of Ethyl 2 : 6-Diphenyl-4-pyridone-3 : 5-dicarboxylate. Pavel Iw. Petrenko-Kritschenko and Joh. Schöttle (*Ber.*, 1910, **43**, 203—206).—The methylation of ethyl 2 : 6-diphenyl-4-pyridone-3 : 5-dicarboxylate in alkaline solution leads to the formation of 2 : 6-diphenyl-1-methyl-4-pyridone-3 : 5-dicarboxylic acid, m. p. 270°, and a mixture, m. p. 125—130° (Abstr., 1909, i, 605). By hydrolysing the latter by 7% aqueous alkali and subsequent acidification, an *acid*, $C_{20}H_{15}O_5N$, is obtained, which separates from dilute acetic acid in crystals, m. p. 240° (decomp.), containing $1\frac{1}{2}C_2H_4O_2$, and forms an *ethyl* ester, m. p. 229—230°, which is insoluble in ammonium

hydroxide. The acid is probably 4-methoxy-2 : 6-diphenylpyridine 3 : 5-dicarboxylic acid. C. S.

Anthranil. XVI. Relation of Anthroxanic Acid (2-Anthranilcarboxylic Acid) to Anthranil. Eugen Bamberger and Sven Lindberg (*Ber.*, 1910, 43, 122—127. Compare Abstr., 1909, i, 509, 510, 511).—*o*-Amino- and *o*-nitro-aromatic aldehydes and ketones are converted by mild oxidising and reducing agents respectively into anthranil derivatives. To establish the constitution of anthroxanic acid as anthranil-2-carboxylic acid, $C_6H_4<\overset{N}{\underset{C(CO_2H)}{\overset{|}{\underset{|}{\text{———}}}}}>O$, the behaviour of isatinic acid and *o*-nitrophenylglyoxylic acid has been studied.

By the oxidation of isatinic acid with Caro's reagent, anthroxanic acid, 2 : 2′-azoxybenzoic acid, and *o*-nitrosobenzoic acid are formed. The last product affords strong support to the view that *o*-hydroxylaminophenylglyoxylic acid, $OH\cdot NH\cdot C_6H_4\cdot CO\cdot CO_2H$, is the first intermediate oxidation product.

o-Nitrophenylglyoxylic acid, when reduced by tin and acetic acid, forms anthroxanic acid and a compound, m. p. 127°, probably 1-acetyldioxindole, $C_6H_4<\overset{CH(OH)}{\underset{N(CO\cdot CH_3)}{\overset{|}{\underset{|}{\text{———}}}}}>CO$. E. F. A.

Cinchonic Acid Syntheses. Walther Borsche (*Ber.*, 1910, 43, 267).—A reply to Schiff (this vol., i, 134). R. V. S.

Elimination of Alkyl Radicles and Fission of Organic Bases by means of Cyanogen Bromide and Phosphorus Halides. Julius von Braun (*Festschrift Otto Wallach*, 1909, 313—386).—A résumé of the author's investigations on this subject (compare Abstr., 1904, i, 688, 731, 841, 918; 1905, i, 596, 634, 636, 826; 1906, i, 576; 1907, i, 28, 79, 105, 110, 127, 151, 524, 728, 899, 960; 1908, i, 625, 627, 675, and 685). The following observations have not been recorded previously. Quinoline is converted by cyanogen bromide and water into a crystalline *substance*, m. p. 113°, which probably has the formula $C_6H_4<\overset{CH=\!=\!=CH}{\underset{N(CN)\cdot CH\cdot OH}{\overset{|}{\underset{|}{\text{———}}}}}>$.

Benzoylhexahydrocarbazole and the 4-methyl compound (compare Borsche, Abstr., 1908, i, 365), when acted on by phosphorus chlorides, yield 2-*benzoylaminodiphenyl*, m. p. 102°, and 2′-*benzoylamino*-4-*methyldiphenyl*, m. p. 121°, respectively. W. H. G.

Indigoid Dyes. V. Indigoid Dyes of the Anthracene Series. A. Bezdzik and Paul Friedländer (*Monatsh.*, 1909, 30, 871—878. Compare Abstr., 1909, i, 415, 417).—Isatin chloride and isatinanilide condense with hydroxy-derivatives of anthracene, forming indigoid dyes, which are far more stable towards acids and alkalis than the analogous naphthalene compounds (compare Abstr., 1908, i, 673); for example, 1-keto-2-indoxylanthracene is not decomposed by sodium hydroxide, although the isomeride, 2-keto-1-indoxylanthracene, when similarly treated yields anthranilic acid and 2-hydroxy-

1-anthracenealdehyde. The latter substance has the property of dyeing animal fibres and the skin an intense yellow :

(I.) $\begin{matrix} C_{10}H_6\cdot CO \\ | \\ CH{=}CH \end{matrix}\!>\!C{:}C\!<\!\begin{matrix} CO \\ | \\ NH \end{matrix}\!>\!C_6H_4$ (II.) $\begin{matrix} CH{-}{-}CO \\ \| \\ CH\cdot C_{10}H_6 \end{matrix}\!>\!C{:}C\!<\!\begin{matrix} CO \\ | \\ NH \end{matrix}\!>\!C_6H_4$

1-*Keto*-2-*indoxylanthracene* (I), prepared by the condensation of α-anthrol and isatinanilide in acetic anhydride, crystallises in small, dark blue needles with a bronzy reflex, melts and sublimes with decomposition at a high temperature, and, when reduced with an alkaline solution of hyposulphite, yields an orange-red solution which dyes textile fibres a pure blue.

2-*Keto*-1-*indoxylanthracene* (II), similarly prepared from β-anthrol, forms small, dark blue needles with a coppery reflex, and sublimes with decomposition at a high temperature. 2-*Hydroxy*-1-*anthracenealdehyde*, $C_{15}H_{10}O_2$, crystallises in long, pale yellow needles, m. p. 164°; the *oxime* crystallises in four-sided, pale green plates, m. p. 197° (decomp.); the *phenylhydrazone* forms flat, yellow prisms, m. p. 224—225°; the *aldazine* forms slender, brick-red needles, m. p. above 300°.

5-*Hydroxy*-1-*keto*-2-*indoxylanthracene*, $C_{22}H_{13}O_3N$, prepared from 1 : 5-dihydroxyanthracene and isatin chloride, crystallises in long, slender, dark blue needles; the isomeric 8-*hydroxy*-compound is very similar in properties, but is slightly more green. W. H. G.

Synthesis of Oxazoles and Thiazoles. I. Siegmund Gabriel (*Ber.*, 1910, **43**, 134—138).—By the action of phosphorus pentachloride on benzoylaminoacetophenone, 4-*chloro*-2 : 5-*diphenyloxazole* is formed, and not a chlorinated *iso*quinoline derivative, as might be expected from analogy to the synthesis of dihydro*iso*quinolines from acyl derivatives of phenylethylamine.

ω-Benzoylaminoacetophenone is best prepared from ω-aminoacetophenone hydrochloride by the action of benzoyl chloride in acetic acid solution; it has m. p. 124° [Robinson, Trans., 1909, **95**, 2169, gives 123°]. When heated with two mols. of phosphorus pentachloride, first at the temperature of the water-bath and later to 170°, 4-*chloro*-2 : 5-*diphenyloxazole*, $O\!<\!\begin{matrix} CPh{:}C\,Cl \\ | \\ CPh{:}N \end{matrix}$, is formed, crystallising in slender needles, m. p. 67—68°. When heated with sodium amalgam in alcoholic solution, 2 : 5-diphenyloxazole, $O\!<\!\begin{matrix} CPh{:}C\,H \\ | \\ CPh{:}N \end{matrix}$, is obtained (compare E. Fischer, Abstr., 1896, i, 262). The same compound may be obtained in one operation from benzoylaminoacetophenone when only one molecule of phosphorus pentachloride is used. Similarly, when benzoylaminoacetophenone and phosphorus pentasulphide are heated at 170°, 2 : 5-*diphenylthiazole*, $S\!<\!\begin{matrix} CPh{:}C\,H \\ | \\ CPh{:}N \end{matrix}$, is formed, crystallising in large, rhombic plates, m. p. 103—104°. E. F. A.

Action of Hydrazines on Thiocyanoacetic Acid and its Ethyl Ester. Gustav Frerichs and Paul Förster (*Annalen*, 1910, **371**, 227—257).—The nature of the interaction of thiocyanoacetic acid and phenylhydrazine as described by Harries and Klamt (Abstr.,

1900, i, 413) not being strictly analogous to that of thiocyanoacetic acid and aniline (compare Rizzo, Abstr., 1898, i, 659; Beckurts and Frerichs, Abstr., 1902, i, 763), it was deemed advisable to repeat the work of the first-named investigators, the outcome of which has been the direct negation of many of the statements of these authors.

When phenylhydrazine is added to a cold ethereal solution of thiocyanoacetic acid, a white, crystalline precipitate of *phenylhydrazine thiocarbimidoacetate*, $SCN\cdot CH_2\cdot CO_2H,NH_2\cdot NHPh$, m. p. 92—100°, is obtained, which, when kept for some time, or when boiled with alcohol, passes into *carbaminethioglycollphenylhydrazide*,

$$NH_2\cdot CO\cdot S\cdot CH_2\cdot CO\cdot NH\cdot NHPh,$$

colourless leaflets, m. p. 149°. The latter substance is more readily obtained by the interaction of phenylhydrazine, chloroacetic acid, and potassium thiocyanate in alcoholic solution; when heated at about 155° for an hour, it passes into *dithiodiglycollphenylhydrazide*,

$$S_2(CH_2\cdot CO\cdot NH\cdot NHPh)_2,$$

which crystallises in colourless, glistening leaflets, m. p. 174°, and is also formed by heating carbaminethioglycollphenylhydrazide with 10% aqueous ammonia and treating the solution subsequently with hydrogen peroxide.

When ethyl thiocyanoacetate is boiled with an alcoholic solution of phenylhydrazine, it yields ammonium cyanate, a viscid, oily *substance*, and 3-*anilinothiohydantoin*, $\begin{matrix}CH_2—CO\\ |\\ S\cdot C(NH)\end{matrix}\!\!>\!N\cdot NHPh$, colourless crystals, m. p. 176°, which dissolve in concentrated sulphuric acid and aqueous potassium hydroxide, forming blue and violet solutions respectively; the substance just described is also formed by the action of phenylthiosemicarbazide on chloroacetic acid. The interaction of chloroacetylphenylsemicarbazide and potassium thiocyanate in alcoholic solution leads to the formation of *thiocarbimidoacetylphenylsemicarbazide*, $SCN\cdot CH_2\cdot CO\cdot NPh\cdot NH\cdot CO\cdot NH_2$, small, glistening crystals, m. p. 172—173°, which, when boiled with water, yields 2-*imino*-5-*keto*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazine*, $S\!<\!\begin{matrix}C(NH)\cdot NH\\ |\\ CH_2——CO\end{matrix}\!\!>\!NPh$, crystallising in pale yellow needles, m. p. 161—162°; the crystalline *salts* with the halogen acids, $C_9H_9ON_3S,HX$, were prepared.

Hydrazine hydrate and thiocyanoacetic acid combine, yielding *hydrazine thiocarbimidoacetate*, $SCN\cdot CH_2\cdot CO_2H,N_2H_4$, glistening leaflets, m. p. 87—90°, which undergoes intermolecular rearrangement when kept, passing probably into *carbaminethioglycollhydrazide*,

$$NH_2\cdot CO\cdot S\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

m. p. about 125°, and, when boiled with water, yields a *substance*, which decomposes at 280—290°, and could not be obtained pure. The action of hydrazine hydrate on ethyl thiocyanoacetate leads to the formation of 3 : 3-*bisthiohydantoin*, $\begin{matrix}CH_2—CO\\ |\\ S\cdot C(NH)\end{matrix}\!\!>\!N\cdot N\!<\!\begin{matrix}CO——CH_2\\ |\\ C(NH)\cdot S\end{matrix}$; the same substance is formed by the interaction of bisthiocarbamide (hydrazodicarboxythioamide) and chloroacetic acid; it decomposes without melting at a high temperature.

Carbaminethioglycollphenylhydrazide undergoes the following

changes: (1) when boiled with 10% aqueous ammonia and subsequently treated with hydrochloric acid, it yields *thioglycollphenylhydrazide*, NHPh·NH·CO·CH_2·SH, leaflets, m. p. 112—113°; (2) it is converted by alcoholic potassium hydroxide and methyl iodide under pressure at 100° into *methylthioglycollphenylhydrazide*, $C_9H_{12}ON_2S$, glistening leaflets, m. p. 104—105°; the corresponding *ethyl* compound, $C_{10}H_{14}ON_2S$, forms colourless leaflets, m. p. 84—85°; (3) when heated with alcoholic potassium hydroxide and chloroacetamide, it yields *thiodiglycollamidephenylhydrazide*,

$$NH_2\cdot CO\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot NHPh,$$

colourless leaflets, m. p. 135—136°; (4) with alcoholic potassium hydroxide and ethyl chlorocarbonate it yields *carboxythioglycollphenylhydrazide*, $CO_2H\cdot S\cdot CH_2\cdot CO\cdot NH\cdot NHPh$, m. p. 156—157°; the *potassium* salt has m. p. 212—213°.

The following substances are prepared by methods similar to those just described: *phenylmethylhydrazinethiocyanoacetate*, m. p. 65—68°; *carbaminethioglycollphenylmethylhydrazide*, $C_{10}H_{13}O_2N_3S$, m. p. 145—146°; *methylthioglycollphenylmethylhydrazide*, $C_{10}H_{14}ON_2S$, needles, m. p. 74—75°; *carbethoxythioglycollphenylmethylhydrazide*, $C_{12}H_{16}O_3N_2S$, colourless leaflets, m. p. 82—83°; *carbaminethioglycoll-p-tolylhydrazide*, $C_{10}H_{13}O_2N_3S$, m. p. 164—165°; *thioglycoll-p-tolylhydrazide*, $C_9H_{12}ON_2S$, m. p. 125—126°; *dithiodiglycoll-p-tolylhydrazide*, $C_{18}H_{22}O_2N_4S_2$, glistening leaflets, m. p. 182—183°; *methylthioglycoll-p-tolylhydrazide*, $C_{10}H_{14}ON_2S$, glistening leaflets, m. p. 108—109°; *thiodiglycollamide-p-tolylhydrazide*, $C_{11}H_{15}O_2N_3S$, glistening, pale yellow needles, m. p. 148—149°. W. H. G.

Case of Isomerism. [Acylazoaryl Compounds.] Giacomo Ponzio (*Gazzetta*, 1909, **39**, ii, 535—546).—The author has carried out further investigations on the yellow, white, and red isomerides, $C_{13}H_{10}O_4N_4$, obtained by the action of benzenediazonium acetate on the potassium derivative of ω-dinitrotoluene (Abstr., 1908, i, 482, 582; 1909, i, 443, 681). The results obtained settle definitely the structure of the red isomeride, and render probable the accuracy of that already assigned to the white compound, but do not admit of the structure of the yellow derivative being determined.

For the yellow compound, the author has suggested the formula $NO_2\cdot CPh(NO)\cdot O\cdot N{:}NPh$, which would explain its isomeric change into α-nitro-β-nitroso-α-benzoyl-β-phenylhydrazine (Abstr., 1908, i, 482). On the basis of this formula, Dimroth and Hartmann (Abstr., 1909, i, 66) indicate an analogy between this yellow compound and benzene-*O*-azotribenzoylmethane, obtained by the interaction of the potassium derivative of tribenzoylmethane with benzenediazonium acetate, and suggest that the yellow compound is a true *O*-azo-derivative and not a diazo-derivative. But, apart from the fact that the properties of Dimroth and Hartmann's compound are explained equally well by regarding it as a true diazonium salt (compare Auwers, Abstr., 1909, i, 67), its analogy to the author's yellow compound is not borne out by its behaviour with ethereal hydrochloric acid. Thus, benzene-*O*-azotribenzoylmethane gives benzenediazonium chloride and tribenzoylmethane, whilst the diazobenzene

derivative of ω-dinitrotoluene gives the isomeric compounds, α-nitro-β-nitroso-α-benzoyl-β-phenylhydrazine and ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone, $NO_2 \cdot CPh{:}N \cdot NH \cdot C_6H_4 \cdot NO_2$, treatment with water converting the former of these isomerides into β-nitroso-α-benzoyl-β-phenylhydrazine and leaving the latter unchanged. The formula $NO_2 \cdot CPh(NO) \cdot N{:}NPh$ for the yellow compound (*vide supra*) does not, however, explain its reaction with alcohol, with formation of ω-dinitrotoluene, nitrogen, acetaldehyde, and benzene.

The reactions of the red isomeride are not in accord with the structure, $NPh{:}N \cdot CPh(NO_2)_2$, originally assigned to it (Abstr., 1908, i, 482). Thus, on reduction by means of tin and hydrochloric acid, it yields ammonia, benzoic acid, and *p*-phenylenediamine. By sodium methoxide it is converted into α-dinitrotetraphenyltetrazoline (compare Bamberger and Grob, Abstr., 1901, i, 296). These results indicate that the red compound is not ω-benzeneazo-ω-dinitrotoluene, but ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone (compare Bamberger and Grob, Abstr., 1901, i, 567), and direct comparison confirms this indication. The isomeric change of the yellow compound into ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone consists in the passage of a nitro-group from an aliphatic carbon atom into the para-position of the benzene nucleus, and such a transformation is best explained by regarding the yellow compound as ω-benzeneazo-ω-dinitrotoluene, $NPh{:}N \cdot CPh(NO_2)_2$.

It follows from these results that the compound, m. p. 130—135°, previously described as ω-dinitro-ω-benzeneazo-*p*-xylene, must be regarded as ω-nitro-*p*-tolualdehyde-*p*-nitrophenylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot N{:}C(NO_2) \cdot C_6H_4Me,$$

and that described as ω-dinitro-ω-benzeneazo-*p*-methoxytoluene, m. p. 141—148°, as ω-nitroanisaldehyde-*p*-nitrophenylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot N{:}C(NO_2) \cdot C_6H_4 \cdot OMe.$$

But, in addition to the diazobenzene derivatives of the primary dinitrohydrocarbons, the ortho-substituted diazo-salts are also transformed into red isomerides when dissolved in moist ether, and in this case, too, there takes place transference of a nitro-group from the aliphatic carbon atom to the para-position of the benzene nucleus. So that the compound, m. p. 137° (decomp.), previously described (Abstr., 1909, i, 443) as ω-*o*-tolueneazo-ω-dinitrotoluene must be regarded as ω-nitrobenzaldehyde-*p*-nitro-*o*-tolylhydrazone,

$$NO_2 \cdot C_6H_3Me \cdot NH \cdot N{:}CPh \cdot NO_2,$$

a structure which is confirmed by the fact that it yields benzoic acid, ammonia, and 2 : 5-diaminotoluene on reduction with tin and hydrochloric acid; this compound may also be obtained by the interaction of the sodium derivative of ω-nitrotoluene and *m*-nitro-*o*-toluenediazonium sulphate: $CHPh{:}NO_2Na + NO_2 \cdot C_6H_3Me \cdot N_2 \cdot HSO_4 = NaHSO_4 + NO_2 \cdot C_6H_3Me \cdot NH \cdot N{:}CPh \cdot NO_2$. Further, the compounds described as ω-*o*-chlorobenzeneazo-ω-dinitrotoluene, m. p. 140° (decomp.), and ω-*o*-bromobenzeneazo-ω-dinitrotoluene, m. p. 140° (decomp.) (Abstr., 1909, i, 443), must be regarded as the *o*-chloro-*p*-nitrophenylhydrazone and *o*-bromo-*p*-nitrophenylhydrazone respectively of ω-nitrobenzaldehyde, $NO_2 \cdot C_6H_3Cl \cdot NH \cdot N{:}CPh \cdot NO_2$ and

$$NO_2 \cdot C_6H_3Br \cdot NH \cdot N{:}CPh \cdot NO_2.$$

These results explain the observation that, whilst the ortho-substituted diazonium salts give with moist ether their red isomerides, that is, the corresponding ortho-substituted *p*-nitrohydrazones, para-substituted diazonium salts, under the same conditions, lose two atoms of nitrogen and three of oxygen in the form of nitrous compounds, giving acylazoaryl derivatives, the isomeric acylarylnitronitrosohydrazines being formed as intermediate products : $R{\cdot}C(N_2O_4){\cdot}N_2Ar \longrightarrow R{\cdot}CO{\cdot}N(NO_2){\cdot}NAr{\cdot}NO \longrightarrow R{\cdot}CO{\cdot}N{:}NAr$; the para-position which the nitro-group tends to assume is in these cases occupied. It is found, indeed, that these compounds, by the action of absolute alcohol in the cold, give small yields of red isomerides, the nitro-group entering the benzene nucleus in the ortho-position. The red isomeride, m. p. 153—154° (decomp.), of the *p*-diazotoluene derivative of ω-dinitrotoluene (Abstr., 1909, i, 443) is found to be, not ω-*p*-toluenazo-ω-dinitrotoluene, but ω-nitrobenzaldehyde-*o*-nitro-*p*-tolylhydrazone, $NO_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}N{:}CPh{\cdot}NO_2$; reduction of this compound (which may also be obtained by the interaction of the sodium derivative of ω-nitrotoluene and *m*-nitro-*p*-toluenediazonium sulphate : $CHPh{:}NO_2Na + NO_2{\cdot}C_6H_3Me{\cdot}N_2{\cdot}HSO_4 = NaHSO_4 + NO_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}N{:}CPh{\cdot}NO_2$) with tin and hydrochloric acid gives benzoic acid, ammonia, and 3 : 4-diaminotoluene. Similarly, the compound described as ω-*p*-chlorobenzeneazo-ω-dinitrotoluene (Abstr., 1909, i, 443), m. p. 161° (decomp.), must be regarded as ω-nitrobenzaldehyde-*p*-chloro-*o*-nitrophenylhydrazone,

$$NO_2{\cdot}C_6H_3Cl{\cdot}NH{\cdot}N{:}CPh{\cdot}NO_2,$$

and that described as ω-*p*-bromobenzeneazo-ω-dinitrotoluene as ω-nitrobenzaldehyde-*p*-bromo-*o*-nitrophenylhydrazone,

$$NO_2{\cdot}C_6H_3Br{\cdot}NH{\cdot}N{:}CPh{\cdot}NO_2.$$

That the white isomeride, best obtained by dissolving the diazobenzene derivative of ω-dinitrotoluene in anhydrous benzene, is α-nitro-β-nitroso-α-benzoyl-β-phenylhydrazine, $NO_2{\cdot}NBz{\cdot}NPh{\cdot}NO$, is confirmed by its transformation into benzoylazobenzene, $NBz{:}NPh$ (Abstr., 1909, i, 681). T. H. P.

Passage of the Nitro-group from an Aliphatic Carbon Atom to the Benzene Nucleus. Giacomo Ponzio and R. Giovetti (*Gazzetta*, 1909, 39, ii, 546—556).—The action of the sodium derivative of ω-*iso*nitrophenylacetonitrile on benzenediazonium acetate yields benzeneazo-ω-nitrophenylacetonitrile, $NO_2{\cdot}CPh(CN){\cdot}N{:}NPh$, which, by the passage of the nitro-group to the para-position of the benzene nucleus, undergoes spontaneous transformation into ω-cyanobenzaldehyde-*p*-nitrophenylhydrazone, $CN{\cdot}CPh{:}N_2H{\cdot}C_6H_4{\cdot}NO_2$, and a small proportion of the corresponding *o*-nitrophenylhydrazone. This transformation, which is similar to that observed with the diazobenzene derivative of ω-dinitrotoluene (compare preceding abstract), also takes place with substituted diazo-derivatives, the nitro-group entering the benzene nucleus in the ortho-position in cases where the para-position is occupied. The initial compounds formed from ω-nitrophenylacetonitrile are, however, less stable than those yielded by ω-dinitrotoluene, and undergo isomeric change so rapidly that they

cannot be obtained in the dry state. Still more unstable are the compounds formed by ω-nitrotoluene with diazonium-salts, this reaction always giving ω-nitrobenzaldehydephenylhydrazones. In the latter case, it is a hydrogen atom from the aliphatic carbon atom which converts the group ·N:N· into :N·NH·, whilst in the previous cases it is the hydrogen atom from the para- (or ortho-) position of the benzene nucleus.

Benzeneazo-ω-nitrophenylacetonitrile, $NO_2 \cdot CPh(CN) \cdot N:NPh$, forms a pale yellow, flocculent precipitate.

ω-Cyanobenzaldehyde-p-*nitrophenylhydrazone*,

$$CN \cdot CPh:N \cdot NH \cdot C_6H_4 \cdot NO_2,$$

crystallises in yellow plates, m. p. 208—209°, dissolves in alkali hydroxides, forming intensely violet solutions, and, on reduction by means of tin and hydrochloric acid, yields benzoic and hydrocyanic acids and *p*-phenylenediamine.

ω-Cyanobenzaldehyde-o-*nitrophenylhydrazone*, $C_{10}H_{14}O_2N_4$, crystallises in orange-red, flattened needles, m. p. 187°, gives a reddish-brown coloration when dissolved in alkali hydroxide solution, and yields benzoic and hydrocyanic acids and *o*-phenylenediamine when reduced with tin and hydrochloric acid.

ω-Cyanobenzaldehyde-p-*nitro*-o-*tolylhydrazone*,

$$CN \cdot CPh:N \cdot NH \cdot C_6H_3Me \cdot NO_2,$$

obtained by the isomeric change of *o*-tolueneazo-ω-nitrophenylacetonitrile (prepared by the interaction of the sodium derivative of *iso*nitrophenylacetonitrile and *o*-toluenediazonium acetate), crystallises from benzene in brownish-yellow needles, m. p. 188°, forms intensely violet solutions with alkali hydroxide, and yields benzoic and hydrocyanic acids and 2 : 5-tolylenediamine on reduction.

ω-Cyanobenzaldehyde-o-*nitro*-p-*tolylhydrazone*,

$$CN \cdot CPh:N \cdot NH \cdot C_6H_3Me \cdot NO_2,$$

formed by the isomeric transformation of *p*-tolueneazonitrophenylacetonitrile, crystallises in orange-red needles, m. p. 160°, gives a wine-red coloration with alkali hydroxides, and yields benzoic and hydrocyanic acids and 3 : 4-tolylenediamine on reduction.

ω-Cyanobenzaldehyde-o *chloro*-p-*nitrophenylhydrazone*,

$$CN \cdot CPh:N \cdot NH \cdot C_6H_3Cl \cdot NO_2,$$

prepared from *o*-chlorobenzenediazonium acetate and the sodium derivative of ω-*iso*nitrophenylacetonitrile, forms orange-coloured needles, m. p. 182°, and gives violet-red solutions with alkali hydroxides.

ω-Cyanobenzaldehyde-p-*chloro*-o-*nitrophenylhydrazone*, formed from *p*-chlorobenzeneazonitrophenylacetonitrile by isomeric change, crystallises in brownish-yellow laminæ, m. p. 240°, and gives intensely violet solutions with alkali hydroxides in presence of a small quantity of alcohol.

ω-Cyanobenzaldehyde-o : p-*dinitrophenylhydrazone*,

$$CN \cdot CPh:N \cdot NH \cdot C_6H_3(NO_2)_2,$$

formed by isomeric change of either *o*- or *p*-nitrobenzeneazonitrophenylacetonitrile, crystallises in reddish-brown prisms, m. p. 246° (decomp.), and gives intensely violet solutions with alkali hydroxide in presence of a drop of alcohol. T. H. P.

Limiting Cases between Polymorphism and Isomerism. Roberto Ciusa and Maurice Padoa (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 621—626).—*m*-Nitrobenzaldehydephenylmethylhydrazone forms two modifications, one red and the other yellow, both having m. p. 120—125° (Labhardt and Zembruski, Abstr., 1900, i, 125, found 112°, and Bamberger and Pemsel, Abstr., 1903, i, 286, 112—113°), at which temperature mixtures of the two also melt. The yellow form has the normal molecular weight in freezing benzene, the solution depositing the red modification on evaporation. Certain solvents, such as chloroform and benzene, convert the yellow into the red form, which may also be obtained by strongly cooling solutions of the yellow modification, or by seeding an alcoholic solution of either form with the red crystals. The red modification passes into the yellow on boiling with alcohol or ethyl acetate, on seeding its alcoholic solution with a yellow crystal, or on prolonged immersion in water or alcohol. There is no apparent or spectroscopic difference between solutions of the two products even when these are freshly dissolved. Both forms give with picryl chloride one and the same additive compound, which undergoes a considerable amount of dissociation even in concentrated alcoholic solution, giving the red hydrazone.

p-Nitrobenzaldehydephenylmethylhydrazone also occurs in two forms, one red and the other yellow, both having m. p. 130° (Labhardt and Zembruski, *loc. cit.*, found 132°). In this case, too, each form can be transformed into the other, but the change in colour is less distinct than with the meta-isomeride, and the red modification is very unstable unless stored under special conditions. *o*-Nitrobenzaldehydephenylmethylhydrazone occurs only in a red form, m. p. 90° (Labhardt and Zembruski, *loc. cit.*, found 77°), but *m*-nitroanisaldehyde-*p*-nitrophenylhydrazone, which is yellow when perfectly dry, becomes red immediately in moist air (Abstr., 1907, i, 137).

The criteria given by Wegscheider (Abstr., 1902, ii, 126) are insufficient to indicate whether this phenomenon is a case of isomerism or one of polymorphism. In this and in other cases, the phenomena of polymorphism and of isomerism approach so closely that the existence of a line of demarcation is not evident (compare Fock, this vol., ii, 23). T. H. P.

Pantachromism of Dimethyl- and Diphenyl-violurates. Arthur Hantzsch and Robert Robison (*Ber.*, 1910, 43, 45—68. Compare Abstr., 1909, i, 331, 333, 335).—In addition to the yellow lithium dimethylviolurate (*loc. cit.*, i, 335), a *red* salt, $C_6H_6O_4N_3Li$, has been prepared. It yields carmine-red compounds with 1EtOH and $1H_2O$. The yellow salt becomes red in the presence of traces of water. The solutions of the two lithium salts in pyridine are red, and in phenol, orange-coloured. A yellow compound with phenol, $C_6H_6O_4N_3Li,PhOH$, is described ; it loses phenol when exposed to the air, and forms the red hydrated salt.

When the violet sodium salt is exposed to the air, it absorbs moisture (1 mol.) and becomes red. A *red* anhydrous sodium salt can be prepared by heating the compound containing ethyl alcohol. The

compound with phenol (1PhOH) is yellow, and when heated at 100° with methyl alcohol yields the anhydrous red salt. The blue potassium salt when exposed to the atmosphere yields the violet hydrate ($\frac{1}{2}H_2O$); the corresponding *phenol* compound has a rose-red colour.

The bluish-violet rubidium salt (*loc. cit.*, 334) contains $0{\cdot}5H_2O$, and when boiled with methyl alcohol yields a pure *blue* anhydrous salt; the *phenol* compound has a rose-red colour. The *caesium* salt crystallises from alcohol in deep indigo-blue needles, and yields a rose-red phenoxide. Dimethylvioluric acid and phenol yield a yellow additive compound. Two coloured *silver pyridine* salts, $C_6H_6O_4N_3Ag,C_5NH_5$, have been prepared: a labile *green* salt by the addition of ether to the pyridine solution of brown silver dimethylviolurate, and a stable *bluish-violet* salt obtained when the green salt is left in contact with ether and pyridine.

The *methylamine* salt, $C_6H_7O_4N_3,NH_2Me$, has a rose-red colour, and when exposed to the air yields the yellow acid salt; the *dimethylamine* salt is violet, the *normal trimethylamine* salt is blue, the *acid* salt orange-yellow, and the *tetramethylammonium* salt is blue. The ethylamine salts are very similar. The normal tripropylamine salt could not be isolated; the *acid* salt, $2C_6H_7O_4N_3,NPr_3$, is orange-yellow. The *dibenzylamine* salt exists in a labile red and a stable bluish-violet modification. *Piperidine* yields a stable blue and a labile red salt, $C_6H_7O_4N_3,C_5H_{11}N$. *Pyridine* yields a stable yellow acid salt.

Diphenylvioluric acid was prepared by a modification of Whiteley's method (Trans., 1907, 91, 1330); the pure neutral salts are best prepared in alcoholic solution, as they readily decompose in the presence of aqueous alkalis. They crystallise with alcohol, which can be completely removed by heating the very finely divided salt. The *lithium* and *sodium* salts exist in labile red and stable yellow modifications, and yield red compounds with 1EtOH. The *ammonium* salt forms a violet compound with EtOH. The *normal potassium*, *rubidium*, and *caesium* salts are blue, and the *acid rubidium* and *caesium* salts green; the *magnesium* and *zinc* salts are yellow; the *thallous silver* salts exist in stable green and labile colourless forms. The *acid silver* salt, $C_{32}H_{21}O_8N_6Ag,3H_2O$, has an orange colour. The salts of dimethyl- and diphenyl-violuric acids exhibit both pantachromism and chromotropism. The labile forms of the salts are usually stable when perfectly dry, but pass readily into the more stable forms in the presence of a little water or alcohol. An increase in the depth of colour of the salts is observed as the metallic radicle becomes more positive, and in the case of substituted ammonium salts an increase in depth of colour is observed with an increase in the number of alkyl groups. The addition of phenol to the molecule of the alkali salts results in a diminution of colour, whereas the addition of pyridine produces an increase in colour, except in the case of the compound of silver violurate and pyridine, which is colourless, and to which the formula

$$CO<\begin{matrix}N{:}C(OPy)\\N{:}C(OPy)\end{matrix}>C{:}N{\cdot}OAg$$

is ascribed.

An increase in the depth of colour with an increase in the positive

nature of the metallic radicle is noticed in the case of concentrated aqueous or alcoholic solutions, and also of solutions in non-ionising solvents, such as chloroform or phenol. A negative solvent tends to lessen the depth of colour of the solution of any given salt. Molecular-weight determinations in phenol and ethyl acetate indicate that the different coloured isomeric salts are unimolecular.

The absorption spectra solutions of the acids and of their alkali salts have been measured.

A comparison of the absorption curves for diphenylvioluric acid, its lithium and cæsium salts, and nitroso*iso*propylacetone (Baly and Desch) points to the conclusion that the blue violurates should be represented as nitroso-enolic salts: $CO<^{NR\cdot CO}_{NR\cdot(COMe)}>C\cdot NO$.

The violuric acids as true oximino-ketones are the more completely transformed into the structurally isomeric nitroso-enols the more positive the nature of the metallic radicle present and the solvent.

J. J. S.

Pantachromic Salts of Oximino-oxazolones. Arthur Hantzsch and J. Heilbron (*Ber.*, 1910, 43, 68—82. Compare Hantzsch and Kemmerich, Abstr., 1909, i, 336).—*p*-Bromo- and *p*-methoxy-derivatives of oximinophenyloxazolone yield pantachromic salts with colourless bases. The esters and acyl derivatives on the other hand are only pale yellow. The salts of the bromo-derivative are comparatively stable, and dissolve in various neutral solvents. Molecular-weight estimations in acetone, pyridine, and chloroform indicate that the salts, both ammonium and metallic, are unimolecular in solution. The colours of the salt solutions in non-ionising media increase in depth with the positive nature of the metallic radicle present.

The absorption spectra, both visible and ultra-violet, of the oxazolones and their salts in different solvents have been tabulated. The free acids are true oximino-compounds, and their absorption spectra resemble those of their ethers and acyl derivatives. The phenolic solution of the oximino-compound is distinctly yellow. The ultra-violet spectra of the salts do not differ materially from those of the free acids, but the visible spectra of the salts show characteristic absorption bands which are not present in the spectra of the free acids. The blue solutions of the potassium, rubidium, cæsium, and tetra-alkylammonium salts give practically identical spectra. The conclusion is drawn that the yellow salts derived from feeble bases possess the true oximino-ketone structure, whereas the blue salts derived from strong bases have a nitroso-enolic structure.

p-*Bromophenyloxazolone*, prepared from ethyl *p*-bromobenzoylacetate and hydroxylamine, crystallises in glistening plates, m. p. 118° (decomp.), and reacts with nitrous acid, yielding *oximino*-p-*bromophenyloxazolone*, $C_6H_4Br\cdot C<^{N\text{———}O}_{C(:N\cdot OH)\cdot CO}$, which crystallises as a pale yellow monohydrate. The anhydrous compound has a pure

yellow colour and decomposes at 166°. The salts readily decompose in aqueous alkaline solutions, but are stable in alcoholic solution. The *lithium* salt, $C_9H_4O_3N_2BrLi$, exists in a stable yellow form only; the *sodium* salt forms orange-red needles, which form a pale rose-coloured *monohydrate*. The *potassium* salt exists in a rose-red and a reddish-violet form, and forms a pale red *phenol* compound, $C_9H_4O_3N_2BrK,C_6H_5\cdot OH$. The *acid potassium* salt is yellow. Rose, blue, and violet *rubidium* salts have been prepared; the *acid* salt is golden-yellow, and the *phenol* compound, pale red. Rose-coloured and bluish-violet *caesium* salts, together with pale red *phenol* compound, are described. The *barium* salt, $(C_9H_4O_3N_2Br)_2Ba,4H_2O$, is red, but when dehydrated is orange-coloured. Similar *calcium* and *magnesium* salts have been obtained. The *zinc* salt, $(C_9H_4O_3N_2Br)_2Zn$, is pale yellow, the *lead* salt pale rose, and the *thallium* salt flesh-coloured. A *blue*, an *orange*, and a *flesh-coloured silver* salt have been prepared, and a carmine-red monohydrate; the orange and the blue salts yield the same methyl ether. The silver salts are insoluble in neutral media, but dissolve in pyridine, yielding dichromatic solutions. The following additive compounds are described: $C_9H_4O_3N_2BrAg,2C_5H_5N$, violet; $C_9H_4O_3N_2BrAg,2NH_3$, deep blue; $C_6H_4O_3N_2BrAg,NH_3$, rose; $C_9H_4O_3N_2BrAg,CH_3CN$, carmine-red.

The *ammonium* salt is orange-coloured; the *methylamine, ethylamine, propylamine,* and *benzylamine* salts are rose-coloured; the *dimethylamine* and *diethylamine* salts are salmon-red; the *dipropylamine* salt, orange-coloured; the *dibenzylamine* salt, red; the *trimethylamine* salt, violet; the *triethylamine* salt, bluish-violet; the *tripropylamine* salt is red, and the *quaternary ammonium* salts crystallise in deep blue plates and their solutions resemble those of the alkali salts. The normal *pyridine* and *picoline* salts are pale yellow. The *methyl ether*,

$$C_6H_4Br\cdot C\lessgtr\begin{matrix}C(:N\cdot OMe)\cdot CO\\ N\text{———————}O\end{matrix},$$

forms pale yellow crystals, m. p. 129° (decomp.). The *acetyl* derivative also forms yellow crystals, m. p. 161° (decomp.), and the *benzoyl* derivative decomposes at 167°.

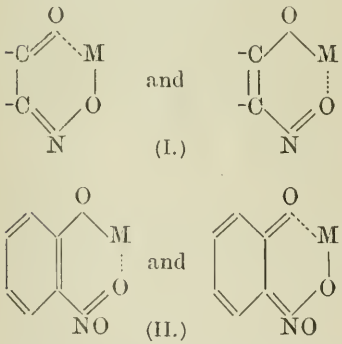
Anisyloxazolone, $OMe\cdot C_6H_4\cdot C\lessgtr\begin{matrix}CH_2\cdot CO\\ N\text{——}O\end{matrix}$, forms crystals with a satiny lustre, and m. p. 140—141° (decomp.). The *oximino*-derivative, $OMe\cdot C_6H_4\lessgtr\begin{matrix}C(:NOH)\cdot CO\\ N\text{—————}O\end{matrix}$, forms a yellow *monohydrate*; the anhydrous compound has a deeper yellow colour, and decomposes at 149°. The salts are not so polychromatic as those of the corresponding bromine derivatives

The following salts are described: *Sodium*, $C_{10}H_7O_4N_2Na$, orange-red; *potassium*, reddish-purple needles; *caesium*, bluish-violet; *ammonium*, red; *silver*, labile rose-coloured and stable blue; $C_{10}H_7O_4N_2Ag,2NH_3$, red. The *methyl ether*, $C_{11}H_{10}O_4N_2$, crystallises in pale yellow needles, m. p. 126°, and when hydrolysed yields *anisylfurazancarboxylic acid*, $OMe\cdot C_6H_4\cdot C\lessgtr\begin{matrix}C(CO_2H):N\\ N\text{——————}O\end{matrix}$, m. p. 99—100°. This acid is undoubtedly formed by the addition of water

and the opening of the oxazolone ring, and the subsequent elimination of methyl alcohol. J. J. S.

Pantachromism of Violurates and Salts of Analogous Oximino-ketones. Arthur Hantzsch (*Ber.*, 1910, 43, 82—91).—The following general conclusions are given: (1) all polychromatic salts are unimolecular in solution, pointing to the isomerism and not polymerism of different coloured salts derived from the same metal; (2) the solutions pass from yellow or orange through red and violet to blue as the positive nature of the metallic radicle increases; (3) the absorption curves of yellow solutions are somewhat analogous to the curves for solutions of the free oximino-ketones in indifferent solvents and to solutions of their acyl and methyl derivatives. Deep blue solutions, on the other hand, show distinct selective absorption, and are optically closely related to blue aliphatic nitroso-compounds. The change in colour is attributed to a chemical change, namely, to the passage from the oximino-ketone form to the nitroso-enolic form: $O{:}\dot{C}\cdot\dot{C}{:}N\cdot OH \longrightarrow OH\cdot\dot{C}{:}\dot{C}\cdot NO$.

All solutions of the salts consist of an equilibrated mixture of the two forms, the proportions of each depending on the positive character of the metallic or substituted ammonium radicle present, and also on the nature of the solvent. It is shown that a mixture of the yellow acetone solution of zinc diphenylviolurate with the blue acetone solution of potassium diphenylviolurate is red and not green.



Leuco-salts yield yellow solutions, indicating a partial conversion into the nitroso-enolic form. The solid salts of orange, red, or purple colour are also regarded as mixed crystals of the two isomeric salts.

When a salt exists in a yellow and a blue form, these are regarded as isomeric in the sense of Werner's valency-isomerism (for example, I).

Similarly, the yellow and red salts of nitrophenol are represented as (II).

The red *aci*-ethers are regarded as analogous to the red salts.

J. J. S.

Purpuric Acid. Arthur Hantzsch and Robert Robison (*Ber.*, 1910, 43, 92—95).—The formula of Piloty and Slimmer and Stieglitz (Abstr., 1904, i, 634) for purpuric acid is analogous to that of the blue violurates: $CO<^{NH\text{---}CO}_{NH\cdot C(OH)}>C\cdot NO$ and $CO<^{NH\text{---}CO}_{NH\cdot C(OH)}>C\cdot N{:}C<^{CO\cdot NH}_{CO\cdot NH}>CO$.

It has not been found possible to prepare coloured ethers or to isolate the pure violuric acid. A method is recommended for the preparation of pure murexide (ammonium purpurate) (compare

Hartley, Trans., 1905, 87, 1981). The values for the electrical conductivity of the pure salt are: $\mu_{256}=51{\cdot}2$, $\mu_{512}=51{\cdot}5$, $\mu_{1024}=51{\cdot}8$, and $\mu_{\infty}=52{\cdot}9$. The conductivity of the system: murexide + HCl = purpuric acid + NH_4Cl has been determined at 0°. The purpuric acid is only slowly transformed into uranil and alloxan, and becomes colourless after three days. The initial value for μ_{512} is 225, but this gradually falls to 167 after twenty-five minutes, and to 21 after three days.

The value μ_{∞} for purpuric acid at 0° has been found to be 248·8 from the equation $\underset{278{\cdot}8}{\mu_{\infty}\,HCl}-\underset{82{\cdot}9}{\mu_{\infty}\,NH_4Cl}+\underset{52{\cdot}9}{\mu_{\infty}\,murexide}=\underset{248{\cdot}8}{\mu_{\infty}\,purpuric}$ acid. The degree of dissociation at 0° and v_{512} is thus 0·9, and $K=0{\cdot}0158$.

Alloxan is not regarded as a quinonoid substance, since it shows only general absorption. J. J. S.

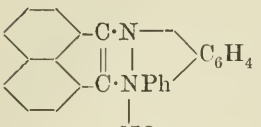
Synthesis of 5 : 7 : 5′ : 7′-Tetrachloroindigotin. Erwin Oberreit (*Compt. rend.*, 1910, 150, 282—283. Compare Danaïla, this vol., i, 137).—The constitution of this substance follows from the fact that it may be prepared from dichloroglycine-*o*-carboxylic acid which has been obtained from 3 : 5-dichloroanthranilic acid. W. O. W.

Quinoline-Red. Eduard Vongerichten and L. Krantz (*Ber.*, 1910, 43, 128—130).—Quinoline-red is obtained by the interaction of molecular proportions of benzotrichloride, quinaldine, and *iso*quinoline in presence of zinc chloride (Hofmann, Abstr., 1887, 380). When oxidised with potassium dichromate, a base is formed, m. p. 125°, which is regarded as *quinolyl* iso*quinolyl ketone*, $C_9H_6N{\cdot}CO{\cdot}C_9H_6N$, since on heating it with concentrated potassium hydroxide, *iso*quinoline and an acid, probably quinaldinic acid, are formed. The base dissolves with a yellow coloration in concentrated acids, and yields an intensely yellow-coloured, crystalline precipitate with phosphorus pentachloride in chloroform solution. The *oxime* forms somewhat grey-coloured, glistening plates, m. p. 245°. A second product of the oxidation is benzaldehyde. E. F. A.

Acenaphthene Series. Fritz Ullmann and Erwin Cassirer (*Ber.*, 1910, 43, 439—445).—As acenaphthene is now a commercial product, the authors have attempted to convert it into dyes or into products from which dyes may be obtained.

A 40% yield of naphthalic acid can be obtained by oxidising acenaphthene with sodium dichromate and sulphuric acid (compare Graebe and Gfeller, Abstr., 1892, 863). Naphthastyril (Ekstrand, Abstr., 1886, 715; 1889, 52) is formed when naphthalimide is treated with sodium hydroxide solution and then with sodium hypochlorite at 15—25°. It reacts with 10% sodium hydroxide solution and *p*-toluenesulphonic chloride, yielding 8-p-*toluenesulphonylamino-naphthoic acid*, $C_7H_7{\cdot}SO_2{\cdot}NH{\cdot}C_{10}H_6{\cdot}CO_2H$, as colourless needles, m. p. 158—159° (decomp.). With acetic anhydride the acid yields p-*toluenesulphonylnaphthastyril*, $C_{18}H_{13}O_3NS$, as straw-yellow, glistening needles, m. p. 174°.

Phenylacenaphthaphenazonium nitrate (annexed formula), obtained from acenaphthenequinone, α-aminodiphenylamine, and acetic and nitric acids, crystallises in glistening, yellow needles. It dyes cotton mordanted with tannin a pale lemon-yellow. The *zincochloride*, $2C_{24}H_{15}N_2ZnCl_3$, forms yellow plates with a brassy lustre; the *dichromate*,



$$(C_{24}H_{15}N_2)_2Cr_2O_7,$$

forms a yellowish-brown, crystalline powder, and the free *base*, $C_{25}H_{15}N_2{\cdot}OH$, a yellowish-green precipitate. The *methyl ether*, $C_{25}H_{18}ON_2$, forms glistening, yellow crystals, m. p. 180—185°.

3-*Chlorophenylnaphthaphenazonium nitrate*,

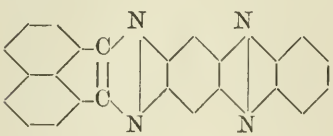
$$C_{10}H_6\langle\begin{matrix}C{\cdot}N\\ \|\ \ |\\ C{\cdot}NPh(NO_3)\end{matrix}\rangle C_6H_3Cl,$$

obtained from acenaphthenequinone and 5-chloro-2-aminodiphenylamine, forms yellow needles, and dyes cotton mordanted with tannin a yellowish-green. The *methyl ether*, $C_{25}H_{17}ON_2Cl$, forms pale green, glistening plates, and has m. p. 200—220°.

2-*Aminophenyl-acenaphthaphenazonium chloride*,

$$C_{10}H_6\langle\begin{matrix}C{\cdot}N\\ \|\ \ |\\ C{\cdot}NPhCl\end{matrix}\rangle C_6H_3{\cdot}NH_2,$$

crystallises in deep violet-coloured needles, and dyes mordanted cotton Bordeaux-red. The *nitrate*, $C_{24}H_{16}O_3N_4$, crystallises in violet plates. The *acetyl* derivative,



$$C_{26}H_{18}ON_3Cl,$$

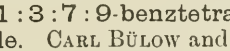
crystallises in long, red needles.

Acenaphthaphenazineazine (annexed formula), obtained by condensing acenaphthenequinone and 2:3-diaminophenazine in acetic acid solution, crystallises in red needles, which are not molten at 320°.

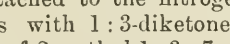
J. J. S.

Methylene-Blue. Paul Landauer and Hugo Weil (*Ber.*, 1910, **43**, 198—203).—Dürrschnabel has shown (*Diss.*, Giessen, 1907) that indamines, oxazines, thiazines, and other para-quinonoid substances are converted by sulphurous acid or hydrogen sulphite into sulphonated leuco-compounds, whilst ortho-quinonoid substances, such as the indulines and safranines, are not reduced, and usually form sparingly soluble sulphites. The authors find that phenylhydrazine acts in a similar way. Methylene-blue, suspended in alcohol, is treated with phenylhydrazine at the ordinary temperature; after half an hour's warming on the water-bath, the system is allowed to cool in carbon dioxide or coal gas. Nitrogen is evolved, and leuco-methylene-blue, m. p. 185°, is obtained in yellow needles. The leuco-compound is stable in dry oxygen, and in the presence of alkaline oxidising agents can be directly acetylated by acetic anhydride, and yields a yellow *sodium* salt with alcoholic sodium ethoxide. Methylene-green by similar treatment yields brown needles of *nitroleucomethylene-blue*, $C_{16}H_{18}O_2N_4S$, m. p. 146—147°. C. S.

Synthesis of Hetero-condensed, Heterocyclic Compounds with Two Nuclei. Derivatives of 2-Methyl-1 : 3-triazo-7 : 0'-pyrimidine [2-Methyl-1 : 3 : 7 : 9-benztetrazole] from 5-Amino-2-methyl-1 : 3 : 4-triazole. Carl Bülow and Karl Haas (*Ber.*, 1910, 43, 375—381. Compare Abstr., 1909, i, 614, 615 (and Errata), 1470; this vol., i, 80, 81).—5-Amino-2-methyl-1 : 3 : 4-triazole contains a labile hydrogen atom attached to the nitrogen next the basic group. Accordingly, it interacts with 1 : 3-diketones, forming di- and tri-alphyl or aryl derivatives of 2-methyl-1 : 3 : 7 : 9-benztetrazole, or with keto-esters, forming methyl benztetrazolehydroxylic acid derivatives.

2 : 4 : 6 - *Trimethyl* - 1 : 3 : 7 : 9 - *benztetrazole*, 

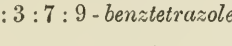
prepared by interaction of the aminotriazole with acetylacetone, forms colourless needles, m. p. 141—142°.

2 : 4 : 5 : 6-*Tetramethyl*-1 : 3 : 7 : 9-*benztetrazole*, 

obtained in a similar manner from methylacetylacetone, has m. p. 116—117°.

4-*Phenyl*-2 : 6-*dimethyl*-1 : 3 : 7 : 9-*benztetrazole* forms colourless, radially grouped, long, thin prisms, m. p. 110—111°.

4-*Hydroxy*-2 : 6-*dimethyl*-1 : 3 : 7 : 9-*benztetrazole*,



obtained by boiling aminomethyltriazole with ethyl acetoacetate in glacial acetic acid solution, separates in glistening crystals, m. p. above 280°. This and the following compounds are acidic, forming salts with alkalis. These react neutral in aqueous solution, and give amorphous or crystalline precipitates with salts of the heavy or alkaline-earth metals. Thus the *lead* salt forms short plates; the *copper* salt, bright green needles; the *zinc* salt, stellar aggregates of needles; the *calcium* salt, glistening needles.

4-*Hydroxy*-2 : 6-*dimethyl*-5-*ethyl*-1 : 3 : 7 : 9-*benztetrazole*, prepared from ethyl ethylacetoacetate, has m. p. 262°, and forms soluble neutral salts, which are not decomposed by carbon dioxide.

4-*Hydroxy*-6-*phenyl*-2-*methyl*-1 : 3 : 7 : 9-*benztetrazole*, obtained from ethyl benzoylacetate, forms long, colourless needles, which do not melt at 293°. E. F. A.

Yellow and Red Forms of Salts and Hydrates of Hydroxy-azo-derivatives. Arthur Hantzsch and Philip W. Robertson (*Ber.*, 1910, 43, 106—122. Compare Tuck, Trans., 1907, 91, 450; Gorke, Köppe, and Staiger, Abstr., 1908, i, 477).—The salts of hydroxy-azo-compounds appear to exist in yellow and red modifications similar to the yellow and red salts of nitrophenols. It is only in the case of silver salts that yellow and red isomeric salts have been obtained from the same compound. Salts of the type $R{\cdot}N_2{\cdot}C_6H_4{\cdot}OM + 0{\cdot}5MeOH$ (EtOH, $CH_3{\cdot}CO_2Et$, $COMe_2$, or C_5H_5N) are common; they are orange-coloured, and are regarded as compounds of 1 mol. of red salt, 1 mol. of yellow salt, and 1 mol. of the crystallising medium. When the last is removed, they yield red or yellow salts, or, sometimes, orange-coloured salts.

The following table gives the colours of the salts of four hydroxyazo-compounds :

	Benzene-azophenol.	*p*-Chlorobenzene-azophenol.	*p*-Bromobenzene-azophenol.	Benzene-azo-*o*-di-bromophenol.
H.....	Yellow	Yellow	Yellow	Orange
Li	Pale yellow	Pale yellow	Pale yellow	Pale yellow
Na	Orange	Orange	Orange	Yellow
K.....	Red	Pale red	Red	Orange
Rb	Dark red	Orange	Red	Orange
Cs	Pale red	Red	Red	Orange
Ag	Yellow (stable) / Red (labile)	Yellow (stable) / Red (labile)	Yellow (stable) / Red (labile)	Red

It is noticeable that the lithium salts are paler in colour than the original hydroxy-derivatives, and that, as a rule, the caesium salts are paler than the rubidium.

The hydrates of hydroxyazo-compounds also appear as representatives of two chromo-isomeric series.

The following are the colours of the hydroxyazo-compounds and of their hydrates (0·5 or 1 mol. H_2O) : *o*-Chlorobenzeneazophenol, red, yellow ; meta-compound, yellow, red ; para-compound, yellow, yellowish-red ; *o*-bromobenzeneazophenol, red, yellow ; meta-compound, yellow, red ; para-compound, yellow, red ; *o*-toluneazophenol, yellow, yellow ; meta-compound, yellow, yellow ; benzeneazo-*m*-cresol, yellow, yellow ; *m*-chlorobenzeneazo-*m*-cresol, yellow, red ; *o*-toluneazo-*m*-cresol, yellowish-red, yellowish-red ; benzeneazo-*o*-chlorophenol, yellowish-red (labile), yellow (stable), yellowish-red. The last-mentioned colour in each case refers to that of the hydrate.

The determinations of the absorption spectra and of the molecular extinctions of solutions of the salts and hydrates show that the yellow and red forms are not polymorphous or polymeric. The solutions in indifferent solvents have much the same colours as the solid salts. The nature of the solvent also affects the colour of the solutions, the more positive the nature of the solvent (namely, pyridine) the deeper the colours. These solutions of salts of hydroxyazo-compounds are regarded as equilibrium mixtures of yellow and red salts, just as in the case of the violurates. From such solutions the orange-coloured additive compounds (1 mol. yellow, 1 mol. red, 1 mol. solvent) separate, as they are sparingly soluble. All these solid additive compounds have practically the same colour, so that the effect of different solvents on the solids is practically nil ; since, however, the solutions have different colours it is probable that the relative amounts of red and yellow salts in the different solutions vary considerably. The increase in colour of the salts, as compared with the free hydroxy-compounds, indicates that salt formation as a rule favours the formation of the red form. It is shown that mere salt formation (Gorke) has not necessarily an auxochromic effect, since lithium salts are paler than the free hydroxy-compounds, and dipropylamine salts in some cases give absorption curves exactly analogous to those of the free hydroxy-compounds.

The following structural valency formulæ are suggested for the yellow and red forms :

where the dotted lines represent subsidiary valencies.

The following values for the molecular extinctions ($\lambda = 546$) of hydroxyazobenzene and its salts in different media at 15° and $V = 200$ are given :

Rubidium salt in pyridine 510, in ethyl acetate 81, in alcohol 44 ; cæsium salt in alcohol 24, in benzene + 4% alcohol 18, in hexane + 4% alcohol 14 ; lithium salt in ether 12 ; dipropylamine salt + 100 mols. dipropylamine in benzene 9 ; hydroxyazobenzene in carbon tetrachloride 8, in chloroform 7, in pyridine 7, in benzene 7, in alcohol 4. The values for the molecular extinctions ($\lambda = 546$) for salts of dibromohydroxyazobenzene at 15° and $V = 400$ are :

Solvent.	Li.	Na.	K.	Rb.	Cs.
Ether	15	17	18	18	—
Alcohol	39	37	35	35	36
Pyridine.....	140	179	180	210	220

J. J. S.

Formation and Decomposition of Symmetrical Bisazocompounds of Ethyl Arylhydrazonemesoxalylbishydrazoneacetoacetates and of Ethyl Malonylbishydrazoneacetoacetate. Carl Bülow and C. Bozenhardt (*Ber.*, 1910, **43**, 234—242).—Ethyl malonylbishydrazonebenzeneazoacetoacetate reacts with one molecule of benzenediazonium chloride, yielding ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate with 72% yield (compare Abstr., 1908, i, 253). In addition, small quantities of ethyl benzeneazoacetoacetate, *cyclo*malonylhydrazide, and 4-benzeneazo-3-methyl-5-pyrazolone are formed. Ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate, when warmed with phenylhydrazine, decomposes into 4-benzeneazo-1-phenyl-3-methylpyrazolone (orange needles, m. p. 154—155° ; yield 85%), 4-*benzeneazopyrazolidone* (m. p. 266°), and hydrazine. When boiled with dilute potassium hydroxide, it yields 4-benzeneazo-3-methyl-5-pyrazolone and mesoxalic acid-phenylhydrazone ; whilst by the action of boiling acetic acid 4-benzeneazo-3-methyl-5-pyrazolone, ethyl benzeneazoacetoacetate, and 4-benzeneazo-3 : 5-pyrazolidone are produced. Dimethyl mesoxalatephenylhydrazone (compare Abstr., 1905, i, 90), when treated with hydrazine hydrate, yields *mesoxalylphenylhydrazonedihydrazide*, m. p. 164°. The *diacetyl* derivative has m. p. 246—247°. The dihydrazide condenses with ethyl benzeneazoacetoacetate, giving ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate, the constitution of which is confirmed by this mode of preparation. The above dihydrazide when boiled with acetic acid also yields 4-benzeneazo-3 : 5-pyrazolidone of m. p. 266°, already mentioned. Ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate is also produced by condensing equimolecular quantities of benzenediazonium chloride and *ethyl malonylbishydrazonebenzeneazoacetoacetate*. The latter is

formed in 80% yield by the condensation of 2 molecules of ethyl benzeneazoacetoacetate with malonyldihydrazide. It is decomposed by boiling alcohol into ethyl malonate and 4-benzeneazo-3-methyl-5-pyrazolone. On heating, it melts at 128°, then gas is evolved, and the mass solidifies, melting again at 217—218°. In this process the theoretical quantity of alcohol is evolved, and the residue consists of 4-benzeneazo-3-methyl-5-pyrazolone and 1 : 1-*malonylbis*-4-*benzeneazo*-3-*methyl*-5-*pyrazolone* (compare Abstr., 1907, i, 986), m. p. 225·5°. On boiling with potassium hydroxide or pyridine, the latter yields 4-benzeneazo-3-methyl-5-pyrazolone and malonic acid.

Ethyl malonylbishydrazoneacetoacetate yields with 3 molecules of *p*-diazotoluene chloride, *ethyl*-p-*tolylhydrazonemesoxalylbishydrazone-toluene*-p-*azoacetoacetate*, orange needles, m. p. 209—210°. By the condensation of malonyldihydrazide with ethyl toluene-*p*-azoaceto-acetate, *ethyl malonylbishydrazonetoluene*-p-*azoacetoacetate*, orange needles, m. p. 114—115°, is produced. R. V. S.

Azo-dyes derived from 2 : 4-Dimethylpyrrole and Hæmopyrrole. Leon Marchlewski and J. Robel (*Ber.*, 1910, **43**, 260—266 *).—For the purpose of comparison with the azo-dyes obtained from hæmopyrrole and chlorophyllpyrrole, the authors have investigated the diazotisation of dimethylpyrrole. In addition to the monoazo-derivative of Plancher and Soncini (Abstr., 1901, i, 432), they have obtained small quantities of a *substance*, $C_{24}H_{25}N_6Cl$, which they suppose to have the formula : $(N_2Ph{\cdot}C_6H_7N{\cdot}C_6H_7N{\cdot}N_2Ph)HCl$. It crystallises in well-developed red needles having a metallic lustre, and it is only slightly soluble in most solvents. In physical characteristics (including the absorption spectrum) the substance shows similarity to the azo-derivative of hæmopyrrole. R. V. S.

Reduction of Nitroso-derivatives of Acetyl- and Benzoylhydrazobenzene. Louis Nomblot (*Compt. rend.*, 1910, **150**, 338—339).—*Nitrosoacetylhydrazobenzene*, NAcPh·NPh·NO, obtained by adding ethyl nitrite to acetylhydrazobenzene suspended in alcohol, occurs in yellow prisms, m. p. 65°. The corresponding *benzoyl* derivative crystallises in pale yellow leaflets, m. p. 116·5°. The action of reducing agents on these two substances has been studied. An alcoholic solution of hydrazine hydrate converts them into the corresponding acidylhydrazobenzene, with liberation of ammonia. Aluminium amalgam gives aniline, together with acetanilide or benzanilide. Zinc dust in presence of acetic acid at 0—5° gives no reduction products. Under no conditions were triazan derivatives obtained. W. O. W.

[Preparation of *p*-Aminophenyl-2-azimino-5-naphthol-7-sulphonic Acid.] Gesellschaft für Chemische Industrie in Basel (D.R.-P. 214658).—p-*Aminophenyl*-2-*azimino*-5-*naphthol*-7-*sulphonic acid*, a grey, crystalline powder sparingly soluble in water and employed in the production of Bordeaux-red dyes, is prepared by the following series of operations:

1-Chloro-2 : 4-dinitrobenzene is condensed with β-naphthylamine-

* and *Bull. Acad. Sci. Cracow*, 1910, *A*, 1—8.

5 : 7-disulphonic acid, yielding 2 : 4-dinitrophenyl-β-naphthylamine-5 : 7-disulphonic acid; this is reduced with sodium sulphide and ammonium chloride to p-*nitro*-o-*aminophenyl*-β-*naphthylamine*-5 : 7-*disulphonic acid*, the *disodium* salt of which forms red, crystalline leaflets. This substance is treated with sodium nitrite in the presence of sulphuric acid, and the resulting *nitroazimino*-compound reduced with iron filings to p-*aminophenyl*-2-*aziminonaphthalene*-5 : 7-*disulphonic acid*, grey needles, which, on heating with sodium hydroxide solution at 180—190°, yields the foregoing naphtholsulphonic acid.

F. M. G. M.

Azoarylhydrazinesulphonic Acids. Julius Tröger and A. Westerkamp (*Arch. Pharm.*, 1909, **247**, 657—698).—The hydrazinesulphonic acid, obtained by the action of sulphur dioxide on aqueous benzenediazonium sulphate (Abstr., 1904, i, 118; 1906, i, 120, 993, 994), has been synthesised by Troeger and Puttkammer (Abstr., 1907, i, 263) by converting diazotised aminoazobenzene into azobenzenediazosulphonate, and reducing the latter by ammonium sulphide:

$$N_2Ph\cdot C_6H_4\cdot NH_2 \longrightarrow N_2Ph\cdot C_6H_4\cdot N_2Cl \longrightarrow N_2Ph\cdot C_6H_4\cdot N_2\cdot O\cdot SO_2K$$
(Labile salt.)

$$\longrightarrow N_2Ph\cdot C_6H_4\cdot N_2\cdot SO_3K \longrightarrow N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H.$$
(Stable salt.)

This synthetic process has now been applied to numerous aminoazo-compounds, whereby hydrazinesulphonic acids are obtained, which are red, blue, violet, or brown; they are best purified by means of their salts with aromatic amines, and are reduced by stannous chloride and hydrochloric acid in the sense of the equation:

$$N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H + 6H + H_2O = NH_2Ph + NH_2\cdot C_6H_4\cdot NH_2 + NH_3 + H_2SO_4,$$

a monoamine and a diamine always being formed. When heated with alcoholic hydrogen chloride and an aldehyde or ketone, the hydrazinesulphonic acids lose the sulphonic acid group, and are converted into hydrazones which form coloured salts with the hydrochloric acid.

4-Amino-*o'm*-azotoluene thus yields a reddish-brown o'm-*azotoluene*-4-*hydrazinesulphonic acid*, $C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot NH\cdot NH\cdot SO_3H$ (the *potassium* and *barium* salts are described; the p-*toluidine* salt,

$$C_{14}H_{15}N_4\cdot SO_3\cdot NH_3\cdot C_7H_7,$$

m. p. 158°, forms yellow needles), which yields *o*-toluidine and 1 : 2 : 5-tolylenediamine by reductive fission, and in the presence of alcoholic hydrogen chloride reacts with salicylaldehyde to form o-*hydroxybenzylidene*-o'm-*azotoluene*-4-*hydrazone*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OH,$$

m. p. 130—131° (the *hydrochloride*, $C_{21}H_{21}ON_4Cl$, forms violet needles, and the *sulphate*, blue needles with a green reflex), with *p*-nitrobenzaldehyde to form a similar *hydrazone*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2,$$

m. p. 158°, with *p*-methoxybenzaldehyde to form the reddish-yellow

hydrazone, $C_{22}H_{22}ON_4$, m. p. 147°, and with benzaldehyde to form an orange-red *hydrazone*, $C_{21}H_{20}N_4$, m. p. 160°.

4-Amino-*mp'*-azotoluene yields reddish-brown, amorphous mp'-*azotoluene*-4-*hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, the p-*toluidine* salt of which, m. p. 183°, forms yellow needles; the *hydrazone*, $C_{22}H_{22}ON_4$, m. p. 148°, from *p*-methoxybenzaldehyde forms golden-yellow leaflets; the *hydrazone*, $C_{21}H_{20}ON_4$, m. p. 120—121°, from salicylaldehyde forms red prisms, and the *hydrazone*, $C_{21}H_{19}O_2N_5$, m. p. 176—177°, from *m*-nitrobenzaldehyde is a reddish-brown, crystalline powder.

op'-*Azotoluene*-4-*hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, obtained from 4-amino-*op'*-azotoluene, is a dark reddish-brown, amorphous powder; the p-*toluidine* salt, m. p. 171°, forms reddish-yellow needles. mp'-*Azotoluene*-6-*hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, is an indigo-blue, amorphous powder obtained from 6-amino-*op'*-azotoluene; the p-*toluidine* salt has m. p. 154°, and the *aniline* salt has m. p. 139°. *Benzeneazo*-p-*toluene*-4-*hydrazinesulphonic acid*,

$$C_{13}H_{14}O_3N_4S,$$

is a dark red, amorphous powder, which forms a yellow, crystalline p-*toluidine* salt, m. p. 170° (decomp.), and a p-*xylidine* salt, m. p. 175° (decomp.). *Benzeneazo*-p-*xylidine*, $N_2Ph\cdot C_6H_2Me_2\cdot NH_2$, m. p. 104—105°, obtained by the slow addition of diazotised aniline hydrochloride to an alcoholic solution of *p*-xylidine and treatment of the resulting hydrochloride with ammonium hydroxide, separates from dilute alcohol in golden leaflets, and from petroleum and benzene as a deep orange, crystalline powder, and forms a *nitrate* crystallising in long, blue needles, a violet *hydrogen sulphate*, and a golden-yellow *oxalate*. It is converted by the usual processes into *benzeneazo*-2 : 5-*xylene*-4-*hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, a dark red, micro-crystalline powder, the reddish-yellow p-*toluidine* salt of which has m. p. 158°.

Benzeneazo-α-naphthylhydrazinesulphonic acid,

$$N_2Ph\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3H,$$

obtained from benzeneazo-α-naphthylamine, is an amorphous, violet powder, which is best purified by means of its *potassium* salt,

$$C_{16}H_{13}O_3N_4SK,$$

which crystallises in reddish-yellow needles. The acid is reduced by zinc dust and hot acetic acid, yielding aniline and 1 : 4-naphthylenediamine, and reacts with alcoholic hydrogen chloride and aldehydes in the manner mentioned, hydrazones being produced in the form of hydrochlorides; the *hydrazone*, $N_2Ph\cdot C_{10}H_6\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OMe$, m. p. 158—160°, from *p*-methoxybenzaldehyde forms orange needles (*hydrochloride*, deep blue needles); the *hydrazone* from salicylaldehyde has m. p. 205° (*hydrochloride*, bluish-violet needles); the *hydrazone* from *p*-nitrobenzaldehyde has m. p. 172—173° (*hydrochloride*, dark green powder).

In a similar manner, benzeneazo-β-naphthylamine yields *benzeneazo-β-naphthylhydrazinesulphonic acid*, a coffee-coloured, amorphous powder, which is purified through the p-*toluidine* salt, m. p. 165° (decomp.).

2 : 4 : 3' : 5'-*Tetramethylazobenzene*-2-*hydrazinesulphonic acid*,

$$C_6H_3Me_2\cdot N_2\cdot C_6H_2Me_2\cdot NH\cdot NH\cdot SO_3H,$$

obtained from aminoazo-*m*-xylene, is a red, amorphous powder, which forms a p-*toluidine* salt, m. p. 170° (decomp.), *aniline* salt, m. p. 153° (decomp.), and a p-*xylidine* salt, m. p. 176° (decomp.).

α-*Naphthylazo-α-naphthylhydrazinesulphonic acid*,

$$C_{10}H_7\cdot N_2\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3H,$$

obtained from aminoazo-α-naphthalene, is a dark blue substance.

C. S.

The Adsorption of Proteins. Wilhelm Biltz and Hans Steiner (*Biochem. Zeitsch.*, 1909, 23, 27—42).—The adsorption of egg-white by cellulose, iron hydroxide, and kaolin was estimated in varying concentrations of the protein. The amount adsorbed was determined by estimating the nitrogen in the clear solution, after filtration of the adsorbent, by a modification of Kjeldahl's method, the amount of ammonia being determined colorimetrically with the use of Nessler's reagent. The adsorption process is not entirely reversible, and the results do not entirely agree with the ordinary adsorption equation. The application of the adsorption formula to the combination of toxin and antitoxin was also investigated ($1 - T/n = \log k + 1/p \log T$, where T is the concentration of the free toxin, and $1 - T$ that of the combined). The results of the neutralisation of tetanolysin and streptolysin by the antilysins, and of the streptolysin by cholesterol, of diphtherotoxin by its antitoxin, of saponin by ox-blood, of cobralysin by antivenin, and other similar reactions were investigated. The results obtained were compared with those calculated from the adsorption equation and Arrhenius' mass reaction equation. Neither of these equations agreed in a satisfactory manner with the results obtained experimentally.

S. B. S.

Composition of the Products of the Alkaline Hydrolysis of Crystalline Egg-albumin. Nogendramohon Gupta (*Monatsh.*, 1909, 30, 767—771).—The products resulting from the hydrolysis of egg-albumin by sodium hydroxide (compare Skraup and Hummelburger, Abstr., 1909, i, 340) have been submitted to careful analysis, with the following results :

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.
Protalbic acid	55·4	7·2	14·3	2·4
Lysalbic ,, ...	52·9	7·0	14·9	1·2
Lysalbinpeptone	46·2	6·6	10·3	1·2

W. H. G.

The Preparation and Properties of Iodo-Mucoids. Gustave M. Meyer (*J. Biol. Chem.*, 1909, 7, 11—16).—Iodo-mucoids were prepared by the action of iodine on tendo-mucoid in a dilute solution of sodium carbonate; they contain approximately 14% of iodine.

W. D. H.

The Relation of Proteins to Crystalloids. I. The Osmotic Pressure of Hæmoglobin and the Laking of Red Blood-corpuscles. Herbert E. Roaf (*Quart. J. exp. Physiol.*, 1910, 3, 75—96).—A simple method is described for the direct measurement of the osmotic pressure of a solution when the solute does not pass

through parchment paper or other suitable membranes. In this way the osmotic pressure of laked corpuscles and crystallised hæmoglobin was measured, and pressures corresponding with the molecular weight of hæmoglobin calculated from other data were obtained if conditions obtain which limit ionisation; but otherwise much higher pressures are reached, and it is suggested that this is due to the ionising of hæmoglobin salts; both acid and alkali increase the pressure, and as with serum proteins, a minimal pressure is found near the neutral point. Many substances lower the osmotic pressure, and thus might help to prevent laking of red corpuscles. Pressures were obtained with corpuscles laked by freezing and thawing up to 282 and 256. If ionisation occurred, the calculated pressure might be as high as 960 mm. of mercury. With such a range of pressure, the osmotic pressure of hæmoglobin should be considered in discussing the laking of corpuscles, but until further experiment has determined the pressures in mixed solutions containing the various crystalloids of the corpuscle, it cannot be decided what part is played by hæmoglobin and how much is due to other factors. W. D. H.

Blood Colouring Matter. William Küster (*Ber.*, 1910, **43**, 370—375).—The compound, $C_{36}H_{36}O_3N_4$, obtained by Küster and Fuchs (Abstr., 1907, i, 572) as a bye-product of the action of aniline on hæmin is also formed in small quantity when acetylhæmin is converted into dehydrochloridehæmin. By the action of concentrated hydrochloric acid under pressure on hæmatin, the organic material partly loses its acid properties and partly undergoes oxidation. Hæmin and hæmatin are regarded as ferric compounds, and the ferric chloride formed oxidises part of the iron-free hæmatin. The oxidation product does not undergo rearrangement to hæmatoporphyrin. When hydrogen bromide is used, the oxidising action of the ferric bromide is neutralised, and hæmatoporphyrin formation takes place. Ten % hydrochloric acid only eliminates 5% of the iron from hæmin at 130°, whereas under similar conditions over 90% of the iron is separated from hæmatin.

Hæmatin is slowly changed by solution in alkali, whereas the fresh solution is completely precipitated by the theoretical quantity of barium chloride. After keeping, a large excess of this is required. Polymerisation to a β-hæmatin takes place on keeping.

The conversion of hæmatin by reducing agents into hæmochromogen is regarded as corresponding with a reduction from the ferric to the ferrous state. Hæmoglobin contains ferrous iron; oxyhæmoglobin, however, contains iron peroxide.

Hæmin forms salts with 3 mols. of alkali hydroxide; dehydrochloridehæmin, salts with 2 mols. These can be dialysed in 1% solution without the dye passing through. Hæmin only takes up 2 mols. of sodium carbonate, and sodium hydrogen carbonate appears in the outer water on dialysis. Precipitates obtained with other metallic salts showed a very varying metal content.

The iron salts dissolve in sodium hydroxide and are acids; seemingly, the second iron atom is attached to the free nitrogen atom.

E. F. A.

Behaviour of Gelatinous Substances or Collains towards Carbon Disulphide. Wl. S. Sadikoff (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1597—1686; *Kolloid. Chem. Beihefte*, 1910, 1, 119—220).—When an alkali acts on glutin in presence of carbon disulphide, "thiohydration" occurs, this consisting of two distinct processes, namely, hydration by the alkali and subsequent addition of carbon disulphide or "thionylation" (compare Abstr., 1907, i, 740). The most characteristic part of the thionylglutin thus obtained is the complex to which the carbon disulphide is added, and which is termed the "receptor." This receptor is extremely indifferent, neither being destroyed by water, reacting with tannin, bromine, aldehydes, or the majority of organic acids, nor being replaced by benzoyl chloride or methyl iodide. It takes up carbon disulphide in neutral, alkaline, or acid media, combines with strong mineral acids, and with acetic and oxalic acids, is substituted by trinitrophenol and "immobilised," or rendered incapable of taking up carbon disulphide, by solutions of sulphates, probably owing to the sulphuric acid formed by adsorptive decomposition of the salts.

In the case of tendo-collagen, the receptor is not homogeneous. The predominating part of it is readily reactive, being replaced by carbonic acid, and by organic and mineral acids, acetic anhydride, benzoyl chloride, bromine, methyl iodide, or aldehydes; it is stable towards the action of heat or water, and is not replaced by picric acid. The lesser part of the receptor is highly inert, is replaceable only by mineral acids and tannin, and is stable towards the action of water, but thermo-labile; this part is not altered by the action of alkali hydroxide. The reactive portion of this receptor would seem to be a primary or secondary amine. T. H. P.

The Scission Products Resulting from the Partial Hydrolysis of Proteins. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1909, 63, 401—404).—From the partial hydrolysis of silk, glycyl-*l*-tyrosine was obtained previously. The present research gives details of the preparation and identification of another dipeptide from the same source, namely, *d*-alanyl-glycine. W. D. H.

Trypsin and Antitrypsin. Kurt Meyer (*Biochem. Zeitsch.*, 1909, 23, 68—92).—Samples of dried pancreatic juice and juice from the small intestine were used in the experiment, and dissolved to give the necessary concentrations as required. The tryptic action was estimated by the Gross-Fuld caseinogen method. The influence of the quantity of kinase on the activation of the trypsinogen was first investigated. The results indicate that the kinase action is of ferment-like character. The grade of activation is not proportional to the amount of kinase, and very small quantities of the latter can activate large quantities of the trypsinogen, provided that sufficient time is allowed for the action. The rate of activation is approximately proportional to the amount of kinase. The greater activity of mixtures containing large amounts of kinase is apparently due to a shortening of the activating process, owing to which the concurrent destruction of the trypsin and kinase becomes less marked. An excess of kinase does not inhibit the activation. The inhibitory

substance of the serum is neither an antikinase nor an anti-trypsinogen. The former possibility is excluded by the fact that the anti-action is not overcome by the addition of excess of kinase, and is also exerted on trypsin which has been obtained from trypsinogen by calcium salts. Antitrypsinogen and antikinase are also excluded by the fact that the inhibitory action of the serum is not increased by allowing it to act on the kinase or trypsinogen alone before mixture, and that the quantity necessary for inhibiting a mixture which is being gradually activated depends on the amount of trypsin actually present at the time of addition.

No antitrypsinogen or antikinase could be obtained by immunisation experiments. The saturation of trypsin by the anti-substance follows the law of multiple proportions. In the fractional saturation of trypsin by the anti-substance, the Danysz phenomenon was observed, namely, the inhibitory action is weaker than if the whole quantity of anti-substance had been added at one time.

Previous treatment of trypsin by antitrypsin did not increase the inhibitory effect. The formation of a non-digesting, but anti-substance binding trypinoid could not be effected. The effect of heating trypsin and the anti-substance was also investigated. The results indicate that antitrypsin is not a negative catalyst, but actually enters into combination with trypsin. No kind of specificity was noted in the case of antitrypsin. S. B. S.

Influence of the Reaction of the Medium on the Filtration of Diastases. Maurice Holderer (*Compt. rend.*, 1909, **149**, 1153—1156).—Details of experiments on extracts of *Aspergillus niger* are given, from which it appears that a porcelain filter is permeable to sucrase when the solution in which this is present is neutral to phenolphthalein; when the solution is neutral to methyl-orange, however, the ferment no longer passes the filter. In order, therefore, to render the extraction of sucrase more complete, it is desirable to have the solution alkaline whilst maceration is in process. W. O. W.

Influence of the Reaction of the Medium on the Filtration of Malt Enzymes. Maurice Holderer (*Compt. rend.*, 1910, **150**, 285—288. Compare preceding abstract).—The enzymes of malt, amylase, dextrinase, and peroxydiastase resemble the diastases already studied in their behaviour when the solutions are filtered through porcelain. Filtration occurs readily when the solutions are neutral to phenolphthalein, but the passage of the enzymes through the filter is inhibited if the medium is neutral to methyl-orange. W. O. W.

Cellase and the Diastatic Decomposition of Cellose. Gabriel Bertrand and Maurice Holderer (*Compt. rend.*, 1909, **149**, 1385—1387).—An attempt to ascertain whether a specific ferment exists capable of hydrolysing cellose. Maltase and sucrase are without action on this substance, whilst a maceration of *Aspergillus niger* converts it completely into dextrose. Preparations of emulsin from almonds, and of emulsin with trehalase from barley or malt, have the same action. W. O. W.

Organic Chemistry.

Action of Magnesium on the Vapours of Organic Compounds. Edward H. Keiser and LeRoy McMaster (*J. Amer. Chem. Soc.*, 1910, 32, 388—391).—Keiser and Breed (Abstr., 1895, i, 405) have shown that when the vapour of an aliphatic alcohol was passed over heated magnesium, a black residue was obtained, which was decomposed by water with evolution of hydrogen and allylene. In a later paper (Keiser, Abstr., 1896, i, 457) an account was given of the action of magnesium on the vapours of other compounds. It was found that if the metal was heated in an atmosphere of carbon monoxide or dioxide, a hard mass was obtained, which gave only small quantities of allylene when treated with water, and the conclusion was therefore drawn that a magnesium compound of allylene was probably present in the black residue.

Attempts have now been made to prove definitely whether the substance which yields the allylene is a magnesium allylide or merely a carbide. Experiments have been made with various classes of organic compounds, including paraffin and benzene hydrocarbons, aliphatic acids and esters, aromatic alcohols, halogen derivatives, acetylene, and cyanogen. In each case the residue obtained was treated with water containing a little ammonium chloride, and the gases evolved were led into an ammoniacal solution of silver nitrate. The silver precipitates were analysed, and the results are tabulated.

In all cases in which the magnesium was heated with the vapour of a compound containing hydrogen, the unsaturated hydrocarbon formed was mostly allylene. When the compound did not contain hydrogen, as in the cases of cyanogen and carbon monoxide, only very small quantities of the unsaturated hydrocarbon were produced, but even then the gas evolved contained some allylene as well as acetylene. This fact seemed to indicate that a carbide is produced which yields allylene on treatment with water. Since, however, it was found that the magnesium powder contained hydrogen, and that only a very small quantity of allylene is obtainable from carbon compounds which do not contain hydrogen, the conclusion is drawn that it is not a carbide, but an allylide, which yields the allylene. This is supported by the fact that when magnesium is heated in acetylene, the black residue on treatment with water gives both allylene and acetylene.

E. G.

The Electrochemical Preparation of Chloroform. B. Wäser (*Chem. Zeit.*, 1910, 34, 141—142).—Chloroform is not obtained in satisfactory yield by the electrolysis of potassium or calcium chloride in presence of alcohol. Barium chloride gives better results, owing to the greater solubility of barium than of calcium hydroxide. A special apparatus is described, in which a porous cylinder surrounds the platinum cathode. The anode is a platinum plate. The cathode

solution is 30 c.c. of hydrochloric acid, D 1·19; the anode solution contains 80 grams of barium hydroxide, 1 gram of barium chloride, and 300 c.c. of water; 30 c.c. of alcohol are then added slowly, the temperature being 50°. Chloroform and alcohol distil off together, the temperature being gradually raised to 70°. The cathode solution is renewed from time to time. The anode current density is about 4 amperes per sq. dm., and the current efficiency is about 35%. Barium carbonate must be absent. Acetone gives a lower yield than alcohol. C. H. D.

Physical and Physiological Properties of Tetrachloroethane and Trichloroethylene. Victor H. Veley (*Proc. Roy. Soc.*, 1910, *B*, 82, 217—225).—*Tetrachloroethane.*—The commercial product was fractionally distilled with a Young's still-head with three bulbs, and the portion of b. p. 147·2° was taken as pure. The densities found were $D_4^4 = 1·6208$ and $D_{17}^{17} = 1·6013_0$. Determinations of the refractive index, μ_D, made at temperatures 15·2° to 17·3°, and corrected to a standard temperature 17°, gave as final value $1·495587 \pm 0·0_56$, calculated by Bessel's function. Gladstone's factor $\mu - 1/d = 0·3095$, and Lorenz's factor $\mu^2 - 1(\mu^2 + 2)d = 0·1824$, which multiplied by the molecular weight give 53·0 and 30·7 respectively.

Trichloroethylene.—One sample after purification boiled at 87·4 ± 0·1 (corr.), and another at 87·55 ± 0·1 (corr.). Practically no hydrogen chloride is given off during distillation. Densities at different temperatures: $D_4^4 = 1·4904_5$, $D_{17·5}^{17·5} = 1·4702_0$, $D_{25·5}^{25·5} = 1·4598_7$, the relative volumes being $V_4 = 1$, $V_{17·5} = 1·0128$, $V_{25·5} = 1·0209$. Refractive index, μ_D, determinations at the same temperatures and above give as final value reduced to 17°, $1·479141 \pm 0·0_53$; Gladstone's factor = 0·326, and Lorenz's factor = 0·193; multiplied by the molecular weight, the results are 42·7 and 25·8 respectively.

Tetrachloroethane is four times more toxic than chloroform, molecule for molecule, but recovery from anæsthesia or paralysis is more regular in the case of the former than in that of the latter.

Trichloroethylene is 1·5 times more toxic than chloroform, molecule for molecule, or 1·36 times weight for weight. Not only the course of abolition, but also of recovery, is much more regular than in the case of chloroform. E. J. R.

Grignard's Reagent and the Barbier-Grignard Reaction. Eyvind Bödtker (*Chem. Zeit.*, 1910, 34, 150).—Attention is called to the fact that the reaction between alkyl iodides and other compounds in presence of magnesium was first employed by Barbier (Abstr., 1899, i, 323), at whose suggestion Grignard studied the reaction, and then devised the reagent in its present form. C. H. D.

The Oxidation Products of Erythritol (*d*-*l*-Erythronic Acid and *d*-*l*-Hydroxyerythronic Acid). Carl Neuberg (*Biochem. Zeitsch.*, 1910, 24, 166—170).—The erythritol was oxidised by nitric acid. The calcium salts were formed, and the concentrated solution of the latter dropped into alcohol. The calcium salt of the hydroxy-acid remains partly in solution, whereas the calcium salt of the

erythronic acid is precipitated. The calcium salt is then dissolved in water, concentrated barium hydroxide added, and the mixture warmed. The remainder of the hydroxy-acid is precipitated. The mother liquor contains the erythronic acid, which is purified by conversion into the copper salt, and finally into the calcium salt again, which latter, when pure, crystallises. The hydroxy-acid is purified by first obtaining it in the form of the basic barium salt (by means of barium hydroxide), and then in the form of the normal barium salt (by means of barium carbonate). The latter is purified by repeated resolution in water and precipitation from aqueous solution by alcohol. S. B. S.

Carnaubon, a Glycerol-free Phosphatide Containing Galactose. Edward K. Dunham and C. A. Jacobson (*Zeitsch. physiol. Chem.*, 1910, 64, 302—315).—This new phosphatide, $C_{74}H_{150}O_{13}N_3P$, prepared from ox-kidney, is soluble in alcohol and almost insoluble in ether. It is a triazomonophosphatide, is free from glycerol, and yields on cleavage, galactose (or amino-galactose), carnaubic, stearic, palmitic, and phosphoric acids and choline. Its constitution appears to be like that of lecithin, the sugar taking the place of glycerol; this allows of more acid groups being united with the molecule. There are probably other similar phosphatides differing in the nature of the sugar and acid groups. W. D. H.

The Simplest Fat, Glyceryl Triformate. Pieter van Romburgh (*Zeitsch. physikal. Chem.*, 1910, 70, 459—461).—Glyceryl triformate has been obtained pure for the first time by the following method. Glycerol was heated repeatedly with 100% formic acid, the excess of acid being distilled off until a mixture rich in the triformin was obtained. The mixture was then cooled in liquid ammonia until a small crystal of the triformin was obtained; on then warming slowly up to 0°, with stirring, the triformin was obtained in colourless crystals, m. p. 18°; $D^{18} = 1{\cdot}320$ (fused ester); $n_D^{18} = 1{\cdot}4412$.

When rapidly heated, the pure ester distils almost unchanged at 266° (762 mm.). When heated very slowly, slight decomposition occurs at 210°. When traces of the lower esters are present, triformin decomposes on heating. It is practically insoluble in, and only slowly hydrolysed by, cold water; it is soluble and fairly rapidly hydrolysed in hot water. It is acted on normally by ammonia and aliphatic amines. G. S.

Preparation of Salts of Dibromobehenic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 215007, 215008, and 215009. Compare Abstr., 1908, i, 122).—The lead and barium salts of dibromobehenic acid have been previously described. *Calcium dibromobehenate* can be prepared (1) by saturating an alcoholic solution of calcium chloride with dry ammonia, filtering from precipitated ammonium chloride, and treating with a solution of dibromobehenic acid in the same solvent; (2) decomposing a very dilute aqueous solution of potassium behenate with calcium chloride; (3) shaking dibromobehenic acid during several days with a saturated solution of calcium hydroxide. It is a colourless, tasteless, odourless powder,

insoluble in water or alcohol, and as a therapeutic agent compares favourably with potassium bromide. *Strontium dibromobehenate* and *magnesium dibromobehenate* are analogously prepared as colourless, tasteless powders, insoluble in water or alcohol. F. M. G. M.

Structure of the Acids of Drying Oils. G. L. Goldsobel (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 55—57).—The structure, $CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$, previously given by the author (*ibid.*, 1906, 38, 182) for linoleic acid is confirmed by the optical properties of the acid, the second formula discussed, $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$, requiring higher molecular refraction and dispersion than those actually found.

Oxidation of the initial products of oxidation of linolenic and *iso*linolenic acids, namely, linusic and *iso*linusic acids, by means of permanganate yields in both cases (1) azelaic acid in almost quantitative amounts, and (2) propionic acid, which forms the principal product of the reaction. Consequently, linusic and *iso*linusic acids have the formula :

$$OH\cdot CHEt\cdot CH(OH)(C_4H_8O_2)\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H,$$

and linolenic and *iso*linolenic acids the formula :

$$CHEt{:}CH(C_4H_6)\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H.$$

As the presence of an allenic linking is excluded, the formula for linolenic and *iso*linolenic acids must be one of the three following :

(1) $CHEt{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$;
(2) $CHEt{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$;
(3) $CHEt{:}CH\cdot CH{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$.

The optical data show that (2) is the correct formula ; this result is confirmed by the observations of Erdmann, Bedford, and Raspe (Abstr., 1909, i, 358). T. H. P.

Oxidation of Methyl Ricinoleate by Ozone. Albin Haller and André Brochet (*Compt. rend.*, 1910, 150, 496—503).—When methyl ricinoleate containing one-tenth of its weight of water is treated with ozone, it forms an *ozonide*, m. p. 80—85°, having the constitution :

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH\cdot CH\cdot[CH_2]_7\cdot C(=O)\cdot OMe,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad O_3$$

An examination of the decomposition products of this substance has established the constitution usually assigned to ricinoleic acid. When added to aqueous sodium carbonate solution the mixture separates into two layers. When acidified, the aqueous layer yields a mixture in which azelaic acid with its monomethyl ester and *β-hydroxynonoic acid*, $CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CO_2H$, have been identified. The latter has been isolated as brilliant lamellæ, m. p. 47—48°, showing $[\alpha]_D$ 2°26′ in alkaline solution. The *silver* salt is crystalline. The optically inactive acid, m. p. 61°, has been prepared by the action of heptaldehyde on the magnesium derivative of ethyl bromoacetate.

In an attempt to separate the above mixture of acids by distillation at 15 mm., *Δ^{α}-nonenoic acid* was obtained, but not in the pure state.

Those portions of the decomposition products which remained insoluble in alkali were found to contain (1) the *methyl* ester of *azelaic*

semi-aldehyde, $CHO\cdot[CH_2]_7\cdot CO_2Me$, which was isolated by means of its *bisulphite* compound and obtained as a liquid, b. p. 140—145°/15 mm. (compare Harries, Abstr., 1906, i, 11; Molinari, *ibid.*, 792). (2) A brown liquid, possibly having the composition

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CHO,$$

since on oxidation it furnished heptoic acid. (3) Methyl stearate and palmitate, together with oily substances of unknown composition.

W. O. W.

Preparation of Calcium Antimony Lactate. Chemische Werke Schuster & Wilhemy (D.R.-P. 216158).—Calcium antimony lactate was previously prepared by treating freshly precipitated antimony oxide with a solution of calcium hydrogen lactate, or a mixture of free lactic acid and calcium lactate. The double salt, $Sb(C_3H_5O_3)_3,Ca(C_3H_5O_3)_2$, can be readily prepared by treating an aqueous solution of antimony fluoride with the requisite amount of normal calcium lactate dissolved in a saturated solution of calcium sulphate, the presence of which is necessary to induce the reaction to take place.

F. M. G. M.

Conductivity Measurements with Dibasic Unsaturated Structure-isomeric Acids. Fritz Fichter and Hans Probst (*Annalen*, 1910, **372**, 69—79. Compare Fichter and Müller, Abstr., 1906, i, 622).—The dissociation constants of four isomeric unsaturated dicarboxylic acids having the formula $C_7H_{10}O_4$ have been measured with the object of ascertaining the effect of the position of the ethenoid linking on the strength of the acid. The acids measured and the dissociation constants at 25° are: allylsuccinic acid, $CH_2{:}CH\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, $K=0{\cdot}0109$; propenylsuccinic acid, $CHMe{:}CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, $K=0{\cdot}00596$; ethylitaconic acid, $CHEt{:}C(CO_2H)\cdot CH_2\cdot CO_2H$, $K=0{\cdot}00356$, and ethylmesaconic acid, $CH_2Et\cdot C(CO_2H){:}CH\cdot CO_2H$, $K=0{\cdot}093$. As usual, the highest value is obtained when the ethenoid linking is situated between the carboxyl groups; in the remaining cases, the strength of the acid increases as the ethylene linking becomes further removed from the carboxyl groups. This relationship does not always exist, however, for Stobbe has shown (Abstr., 1902, i, 461) that γ-ethylidene-γ-methylpyruvic acid, $CHMe{:}CMe\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, is a weaker acid than methylethylitaconic acid, $CMeEt{:}C(CO_2H)\cdot CH_2\cdot CO_2H$.

Propenylsuccinic acid was prepared by boiling the isomeric ethylitaconic acid with aqueous sodium hydroxide; it crystallises in large, colourless, transparent, crystals, m. p. 135°; the *calcium* salt, $C_7H_8O_4Ca$, is crystalline. An attempt to prepare it by distilling γ-methylparaconic-α-acetic acid led to the production of methylethylmaleic anhydride.

γ-Methylparaconic-α-acetic acid,

$$CHMe\begin{<}\begin{matrix}CH(CO_2H)\\ O\text{——}CO\end{matrix}\end{>}CH\cdot CH_2\cdot CO_2H,$$

prepared by reducing ethyl α-acetotricarballylate in alcoholic solution with sodium amalgam, is a crystalline powder, m. p. 175°; the *ethyl* ester, $C_{12}H_{18}O_6$, is a viscid oil, b. p. 198°/13 mm.

W. H. G.

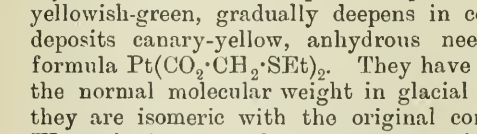
Molybdo-tartrates. P. Quinet (*Bull. Soc. chim.*, 1910, [iv], 7, 105).—The author points out in connexion with Grossmann's claim for priority on this subject (*ibid.*, December 5th, 1909) that his own work (Abstr., 1908, i, 713) does not cover the same ground as that of Grossmann and Pötter (Abstr., 1904, ii, 153; 1906, ii, 211; 1906, i, 799). The erroneous composition assigned to the compound of tartaric acid with sodium molybdate, given in the author's paper (*loc. cit.*) and noted by Grossmann (*loc. cit.*), had already been corrected (*J. phys.*, April, 1909). T. A. H.

The Electrolytic Degradation of the Saccharic Acids from Mono- and Di-saccharides, and also of Certain Hydroxy-amino-acids. Carl Neuberg, L. Scott, and Siegbert Lachmann (*Biochem. Zeitsch.*, 1910, 24, 152—165).—The general scheme of degradation may be represented by the formulæ:

$$OH\cdot CH_2\cdot[CH\cdot OH]_n\cdot CH(OH)\cdot CO_2H \dashrightarrow OH\cdot CH_2\cdot[CH\cdot OH]_n\cdot CHO.$$

In this way the successive degradation of glucoheptonic acid to formaldehyde may be carried out. The electrolysis of the following acids is described: *d*-galactonic acid, *d*-*l*-erythronic acid, *d*-*l*-glyceric acid, and glycollic acid. The products obtained were *d*-lyxose, *d*-*l*-glyceraldehyde, glycolaldehyde, and formaldehyde. *iso*Serine was also electrolysed. Aminoacetaldehyde was not directly isolated in this case, but the products of electrolysis on oxidation with mercuric chloride and sodium hydroxide yielded its oxidation product, pyrazine. Melibionic acid, which was obtained in the form of the calcium salt, was also submitted to electrolysis. A sugar was obtained only in small quantity, and isolated in the form of its *p*-nitrophenylosazone. In most cases the salts of the alkaline earths of the above acids were employed in the electrolysis experiments. S. B. S.

Photo-transformation of an Internal Complex Salt. Ludwig Ramberg (*Ber.*, 1910, 43, 580—584).—Cryoscopic measurements show that platinous ethylthiolacetate (Abstr., 1906, i, 791) is slightly polymerised in aqueous solution. On exposure to sunlight, or to the rays from a Uviol lamp, the aqueous solution, which is slightly yellowish-green, gradually deepens in colour, and after a few days deposits canary-yellow, anhydrous needles or prisms, having the formula $Pt(CO_2\cdot CH_2\cdot SEt)_2$. They have m. p. 204—205°, and possess the normal molecular weight in glacial acetic acid solution, so that they are isomeric with the original compound of m. p. 189—190°. Werner's theory would give two isomerides having the configurations:



T. S. P.

Bimolecular Polymeride of Crotonaldehyde and the Corresponding Acid. Marcel Delépine (*Compt. rend.*, 1910, 150, 394—396. Compare Abstr., 1909, i, 84).—The compound $C_8H_{12}O_2$, formed in small quantity during the preparation of crotonaldehyde by the method already described, may be prepared in larger quantities by

heating in a reflux apparatus for half an hour a mixture of crotonaldehyde with the same weight of hydrochloric acid (D 1·18) and five times its weight of water. The liquid is then distilled. The new aldehyde forms an *azine*, $C_{16}H_{24}O_2N_2$, crystallising in sulphur-yellow prisms, m. p. 168°. On treatment with silver oxide (Abstr., 1909, i, 632) it yields the corresponding *acid*, $C_8H_{12}O_3,H_2O$, m. p. 68—71°. The anhydrous acid, obtained by heating at 60°, has m. p. 85—87°, b. p. 262—264°. The *ethyl* ester has b. p. 107—109°/18 mm., D_4^{20} 1·014, n_D 1·46102. Addition of bromine to an aqueous solution of the acid results in the formation of a *bromohydroxy-acid*, $C_8H_{13}O_4Br$, which crystallises in monoclinic prisms and does not lose water at 100°. W. O. W.

Constitution of the Bimolecular Polymeride of Crotonaldehyde. Marcel Delépine (*Compt. rend.*, 1910, **150**, 535—537. Compare preceding abstract).—The polymeride obtained during the preparation of crotonaldehyde probably has the constitution

$$\begin{matrix} CH_2\text{–}CH{:}C\text{·}CHO \\ | \qquad\quad | \\ CHMe\text{·}O\text{·}CHMe \end{matrix}$$

since on oxidation with chromic acid it forms acetic acid and carbon dioxide, and on treatment with magnesium ethyl bromide yields an *alcohol*, $C_7H_{11}O\text{·}CHEt\text{·}OH$, having a mint-like odour and forming a *monoacetyl* derivative. The *compound*, $C_7H_{11}O\text{·}CH{:}CHMe$, has also been obtained as an agreeably-smelling liquid with a sweet taste, b. p. 82—84°/18 mm.; D_4^0 0·92061; n_D^{20} 1·48567. The ethyl ester of the acid corresponding with the above aldehyde furnishes, on treatment with magnesium ethyl iodide, a *compound*, $C_{12}H_{22}O_2$; this is probably a tertiary alcohol; it has an odour resembling that of pinacone, and does not form an acetyl derivative; b. p. 260°/760 mm., 151—154°/19 mm.; D_4^0 0·9731; n_D^{20} 1·46291.

Refractometric determinations are in agreement with the constitution suggested for the aldehyde. Crotonaldehyde has n_γ^{10} 1·44361. W. O. W.

Alkylation of Aliphatic Ketones by the Use of Sodamide. Albin Haller and Edmond Bauer (*Compt. rend.*, 1910, **150**, 582—589. Compare Abstr., 1904, i, 600; 1905, i, 276; 1909, i, 987).—Pinacolin is readily attacked in ethereal solution by sodamide, forming a soluble sodium derivative, which, on treatment with alkyl iodides, gives rise to a mixture of mono- and di-alkylpinacolins; these can be separated by fractional distillation. Trialkylpinacolins are not produced unless the reaction is carried out in presence of benzene or toluene, when the yield is practically quantitative. The ketones prepared in this way have been reduced to the corresponding secondary alcohols by means of sodium and absolute alcohol. Whilst the mono- and di-alkylpinacolins form oximes and semicarbazones, the trialkyl derivatives do not react with hydroxylamine or semicarbazide. The following compounds are described: the *oxime* of $\beta\beta$-dimethylpentan-γ-one crystallises in lozenges, m. p. 78—80° (compare Wischnegradsky, *Annalen*, 1875, **178**, 104). Nef's *iso*propyl butyl ketone (Abstr., 1900, i, 349) has D_4^2 0·80536, n_D 1·40513, and on reduction yields

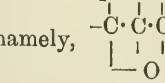
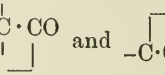
ββδ-trimethylpentan-γ-ol, $CMe_3 \cdot CH(OH) \cdot CHMe_2$, a liquid having an odour like borneol, b. p. 145—148°; the *phenylurethane* has m. p. 79°.

ββδδ-Tetramethylpentan-γ-one, $CMe_3 \cdot CO \cdot CMe_3$, obtained by the action of sodamide on the foregoing ketone, has a camphoraceous odour, b. p. 149—151°, D_4^{25} 0·81992, n_D 1·41702. *ββδδ-Tetramethylpentan-γ-ol*, $CH(OH)(CMe_3)_2$, m. p. 50°, b. p. 165—166°, forms a *phenylurethane*, m. p. 118—119°; the *formyl* derivative has b. p. 185°. *ββδδ-Tetramethylhexan-γ-one*, $CMe_3 \cdot CO \cdot CMe_2Et$, b. p. 172—174°; *ββδδ-tetramethylhexan-γ-ol*, b. p. 187—188°; its *phenylurethane* has m. p. 94—95°. *ββ-Dimethylhexan-γ-one*, $CMe_3 \cdot CO \cdot Pr^{\alpha}$, b. p. 146—148°, D_4^{25} 0·81055, n_D 1·40952; the *oxime* has m. p. 76—77°. *ββ-Dimethylhexan-γ-ol*, b. p. 155—157°, forms a *phenylurethane*, m. p. 70—71°. *ββ-Dimethyl-δ-ethylhexan-γ-one*, $CMe_3 \cdot CO \cdot CHEt_2$, has b. p. 174—176°, D_4^{25} 0·82521, n_D 1·42227, and on reduction yields *ββ-dimethyl-δ-ethylhexan-γ-ol*, $CMe_3 \cdot CH(OH) \cdot CHEt_2$, b. p. 187°; the *phenylurethane* has m. p. 107°. *ββ-Dimethyl-δδ-diethylhexan-γ-one*; $CMe_3 \cdot CO \cdot CEt_3$, b. p. 214—216°; *ββ-dimethyl-δδ-diethylhexan-γ-ol*, b. p. 226—228°, gives a *phenylurethane*, m. p. 110°. *ββδ-Trimethylhexan-γ-one*,

$$CMe_3 \cdot CO \cdot CHMeEt,$$

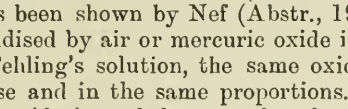
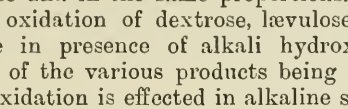
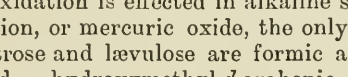
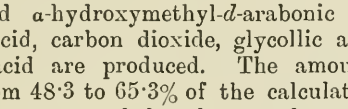
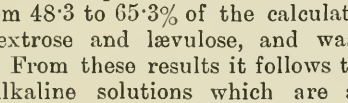
b. p. 155—156°; *ββδ-trimethylhexan-γ-ol*, $CMe_3 \cdot CH(OH) \cdot CHMeEt$, b. p. 169°; the *phenylurethane* has m. p. 78°. *ββε*-Trimethylhexan-γ-one, $CMe_3 \cdot CO \cdot CH_2Pr^{\beta}$, b. p. 157·5—158·5°, forms an oxime, m. p. 77—78° (compare Nef, Abstr., 1902, i, 6). *ββ-Dimethyl-Δ$^{\zeta}$-hepten-γ-one*, $CMe_3 \cdot CO \cdot [CH_2]_2 \cdot CH{:}CH_2$, b. p. 61—64°/14 mm. *ββ-Dimethyl-δ-allyl-Δ$^{\zeta}$-hepten-γ-one*, $CMe_3 \cdot CO \cdot CH(C_3H_5)_2$, b. p. 83—86°/14 mm.

W. O. W.

Relation between the Chemical Constitution and the Optical Rotatory Power of the Sugar Lactones. C. S. Hudson (*J. Amer. Chem. Soc.*, 1910, 32, 338—346).—Data are quoted which show that the aldose sugars and their glucosidic and lactonic derivatives exhibit strong optical rotatory power, whilst the corresponding alcohols and acids have but slight optical activity. It is therefore evident that the lactonic structure causes considerable rotatory power. There are two possible stereochemical configurations for the lactonic ring, namely,  and  . If the rotation is due to this ring, the sign of the rotation must be determined by the position of the ring. This position is determined by the position of the hydroxyl group attached to the γ-carbon atom before the ring was produced. The hypothesis is advanced that dextrorotatory lactones have the lactonic ring on one side of the structure, lævorotatory lactones have it on the other side, and the position of the ring shows the position in which the hydroxyl group was attached to the γ-carbon atom. A list is given of all the sugar lactones of which the structure and specific rotation have been determined, and it is shown that, in all cases, the theory is confirmed.

Suggestions are made with reference to the application of this theory to the determination of the constitution of the sugars.

E. G.

Behaviour of the Ordinary Hexoses towards Hydrogen Peroxide in Presence of Alkali Hydroxides as well as of Various Iron Salts. H. A. Spoehr (*Amer. Chem. J.*, 1910, 43, 227—254).—It has been shown by Nef (Abstr., 1908, i, 5) that when the hexoses are oxidised by air or mercuric oxide in presence of alkali hydroxide or by Fehling's solution, the same oxidation products are formed in each case and in the same proportions. A study has now been made of the oxidation of dextrose, lævulose, and galactose by hydrogen peroxide in presence of alkali hydroxide. It has been found that instead of the various products being obtained which are formed when the oxidation is effected in alkaline solution by means of air, Fehling's solution, or mercuric oxide, the only oxidation products obtained with dextrose and lævulose are formic acid, carbon dioxide, glycollic acid, and α-hydroxymethyl-*d*-arabonic acid, whilst with galactose, formic acid, carbon dioxide, glycollic acid, and α-hydroxymethyl-*d*-lyxonic acid are produced. The amount of formic acid obtained varied from 48·3 to 65·3% of the calculated amount possible in the case of dextrose and lævulose, and was over 80% in the case of galactose. From these results it follows that the only sugars present in the alkaline solutions which are actually selectively oxidised are (1) formaldehyde; (2) glycollaldehyde, which is converted partly into glycollic acid, and partly through glyoxylic acid into carbon dioxide and formic acid; (3) α- and β-*d*-glutose (from dextrose and lævulose),  and  , which give the same glutosone,  , this yielding only α-hydroxymethyl-*d*-arabonic acid,  ; or α- and β-galtose (from galactose), which similarly yield α-hydroxymethyl-*d*-lyxonic acid,  .

α-Hydroxymethyl-d-*arabonic lactone*, $[\alpha]_D$ +72·5°, is a viscous substance. The *phenylhydrazide*, $C_6H_{11}O_6{\cdot}NH{\cdot}NHPh$, m. p. 212—215°, forms lustrous needles. The *brucine* salt, m. p. 186—188°, $[\alpha]_D^{20}$ about −25·7°, and the *calcium* salt, $[\alpha]_D$ about −3·0°, are described.

Brucine α-hydroxymethyl-d-*lyxonate*, m. p. 171—175°, the corresponding *quinine* salt, m. p. 213°, and the *phenylhydrazide*, m. p. 144°, are described.

Experiments have shown that ethylene glycol and glycollic acid,

when oxidised by an alkaline solution of hydrogen peroxide, yield small quantities of formic and carbonic acids, but no oxalic acid.

Morrell and Crofts (Trans., 1899, 75, 786; 1902, 81, 666; 1903, 83, 1290) have studied the oxidation of dextrose, lævulose, and galactose with hydrogen peroxide in presence of ferrous sulphate, and have obtained the hexosone, and glycollic, glyoxylic, and oxalic acids as the oxidation products. These authors have also stated that erythronic (trihydroxybutyric) acid is formed from dextrose and lævulose. On repeating these experiments, erythronic acid could not be obtained, but it is regarded as probable that a ketonic acid or a mixture of ketonic acids containing four carbon atoms is produced. Formic, carbonic, and oxalic acids were isolated. It is considered that the large quantity of oxalic acid (18—27%) produced is due to a direct hydrolysis of polyhexosones, such as $CHO\cdot CO\cdot CO\cdot \overset{OH}{\overset{|}{C}}\overset{H}{\overset{|}{}}—\overset{OH}{\overset{|}{C}}\overset{H}{\overset{|}{}}\cdot CH_2OH$ and $CHO\cdot CO\cdot CO\cdot CO\cdot \overset{OH}{\overset{|}{C}}\overset{H}{\overset{|}{}}\cdot CH_2OH$, formed as the first products of the oxidation. E. G.

Mechanism of the Oxidation of Dextrose by Bromine. Herbert H. Bunzel (*J. Biol. Chem.*, 1910, 7, 157—169. Compare Bunzel and Mathews, Abstr., 1909, i, 289).—Experiments have been made on the oxidation of dextrose with bromine in the presence of dilute sulphuric acid (0·1*N*). The equation used for calculating K was $K = 1/t(a-x)\log.\text{nat.}b(a-x)/a(b-x)$, where a and b are the respective concentrations of the active bromine and sugar at the start, and x the amount of sugar and bromine used up during the time t. This equation gave constant values for K when sodium bromide was added, so that the concentration of the $\overline{Br}$ ions was 0·3*N* in the final mixture; as the bromine in these experiments was only 0·01*N*, the slight increase in the concentration of the $\overline{Br}$ ions during the reaction was negligible. When no sodium bromide was added, K was calculated from the equation:

$$K = \frac{1}{t\left(0{\cdot}05\ (a-b) + \dfrac{(a-b)}{0{\cdot}5 + \text{Br (at start)} + \dfrac{\text{HBr}t_2 - \text{HBr}t_1}{2} - \text{Br}_3}\right)} \log\frac{b(a-x)}{a(b-x)}.$$

Titrations of the acid formed during the reaction indicate that for each molecule of bromine used up a molecule of gluconic acid is formed. Of the total acidity produced during the reaction, it was shown that two-thirds are due to hydrobromic acid and one-third to organic acid (gluconic acid).

The results agree with the view expressed previously, that dextrose in aqueous solution can ionise in two different ways. J. J. S.

The Contraction Occurring when Sucrose is Dissolved in Water and the Density of Sucrose. A. Démichel (*Bull. Assoc. chim. Sucr. Dist.*, 1910, 27, 753—755. Compare Abstr., 1909, ii, 795; this vol., i, 96).—The author calculates the density of sucrose to be 1·581, using for this purpose the tables published by Buisson, and he shows that the contraction taking place when sucrose is dissolved in water may be calculated when the densities of the sucrose, of the water, of the sucrose solution, and the amount of sucrose in the latter, are known. He shows that there is always a contraction and never an expansion. W. P. S.

Contraction Occurring during Solution and the Law of Guéritsch. A. Démichel (*Bull. Assoc. chim. Sucr. Dist.*, 1910, 27, 755—757).—The contraction taking place when sucrose is dissolved may be measured by differences in density, but the author considers that it is more rational to express the contraction as a difference in volume, and gives formulæ for thus calculating the contraction. The law of Guéritsch only allows a more or less imperfect approximation of the contraction to be obtained even in cases where the concentration is such that the phenomenon is most appreciable. W. P. S.

Change of Rotation of Sucrose in Presence of Alkaline Uranyl Salt Solutions. Hermann Grossmann and F. Rothgiesser (*Ber.*, 1910, 43, 676—682. Compare Abstr., 1906, ii, 61).—Sucrose is slowly changed into lævorotatory compounds by the action of uranyl nitrate and sodium hydroxide. Variations in the relative proportions and concentration of sucrose, uranyl nitrate, and alkali are of the greatest influence on the character of the change and on the end point of the reaction. Using 1 mol. of sucrose to 1 mol. of nitrate, the initial rotation is twice that of sucrose; it falls gradually to a negative value. With 2 mols. of nitrate and 15 mols. of sodium hydroxide to 1 mol. of sucrose, the initial rotation is nil, and the final reading $-126{\cdot}7°$. The change is due to the slow hydrolysis of the many complex salts in solution in accordance with the scheme:

$$C_{12}H_{20}O_9(O{\cdot}UrO_2{\cdot}ONa)_2 + 2H_2O \rightleftharpoons C_{12}H_{20}O_9(O{\cdot}UrO_2{\cdot}OH)_2 + 2NaOH$$

$$C_{12}H_{21}O_{10}(O{\cdot}UrO_2{\cdot}ONa) + H_2O \rightleftharpoons C_{12}H_{21}O_{10}(O{\cdot}UrO_2{\cdot}OH) + NaOH.$$

The complex salts are probably strongly dextrorotatory but their products of hydrolysis are highly lævorotatory. Hence an increase in the amount of water displaces equilibrium in favour of the right-hand equation, whilst concentrated sodium hydroxide favours the reverse change. E. F. A.

Configuration of Rhodeose. Emil Votoček (*Ber.*, 1910, 43, 469—475).—Polemical. Rhodeose is the mirror image of fucose, and the configuration is established by the behaviour of rhodeitol towards sorbose bacteria and by the oxidation of rhodeonic acid to *l*-trihydroxyglutaric acid (Votoček, Abstr., 1906, i, 378, 483). The configuration of fucose was accordingly established in 1906 (compare Mayer and Tollens, Abstr., 1907, i, 588). E. F. A.

Additive Products of Hydrogen Cyanide with Rhodeose. Cyrill Krautz (*Ber.*, 1910, 43, 482—488. Compare Votoček, preceding abstract).—By the addition of hydrogen cyanide to rhodeose and hydrolysis, two isomeric rhodeohexonamides are formed: the α-isomeride forms large, colourless prisms, m. p. 206°; the β-isomeride is amorphous, m. p. 197—198°. On hydrolysis with barium hydroxide the *barium* salts of the isomeric rhodeohexonic acids are obtained; that from the α-amide has $[\alpha]_D^{20}$ + 6·88°, and from the β-amide, $[\alpha]_D^{20}$ − 1·49°. *α-Rhodeohexonic acid* is rapidly converted into the lactone, and shows $[\alpha]_D^{20}$ − 30·25° in solution. The salts are amorphous and deliquescent, with the exception of the *barium* and *lead* compounds. *β-Rhodeohexonic acid* gives $[\alpha]_D^{20}$ − 44·25° in solution; the salts are similar to those of the α-isomeride. The *lactone* of the α-acid separates in large, well-formed prisms of sweet taste and neutral reaction, m. p. 129—131°, $[\alpha]_D^{20}$ − 34·8°. The *lactone* of the β-acid reacts faintly acid, tastes sweet, m. p. 115°, $[\alpha]_D^{20}$ − 40·6°. The *α-phenylhydrazide* crystallises in lustrous, silver plates, m. p. 231° (decomp.); the *β-phenylhydrazide* is a glistening, yellow compound, m. p. 211° (decomp.).

The lactones on reduction with sodium amalgam in faintly acid solution at − 5° form the corresponding rhodeohexoses. *α-Rhodeohexose* is a microcrystalline substance, m. p. 125—126°, $[\alpha]_D^{20}$ + 11·96°; *β-rhodeohexose* is amorphous.

The following derivatives were prepared by the usual methods from α-rhodeohexose: The *phenylhydrazone* forms yellow plates, m. p. 150°; the p-*bromophenylhydrazone* is a colourless powder, m. p. 173°; the *phenylmethylhydrazone* forms colourless plates, m. p. 188°; the *phenylosazone* separates in golden-yellow needles, m. p. 231°; the p-*bromophenylosazone* is similar, m. p. 219°.

Of β-rhodeohexose, the *phenylhydrazone* crystallises in colourless plates, m. p. 131—137°; the p-*bromophenylhydrazone* is colourless, m. p. 145°; the *phenylmethylhydrazone* forms silvery, glistening tablets, m. p. 163°; the *phenylosazone* is a citron-yellow powder, m. p. 213°; the p-*bromophenylosazone* is an orange-yellow powder, m. p. 200°.

α- and β-Rhodeohexone lactones are mutually interconvertible when heated in aqueous solution with pyridine at 150°. E. F. A

Acetylation of Cotton Cellulose. Carl G. Schwalbe (*Zeitsch. angew. Chem.*, 1910, 23, 433—441).—A résumé of the different methods of acetylation of cellulose is given. Mork, Little and Walker (Amer. Pat., 709922) use aromatic sulphonic acids instead of mineral acids as catalysts. The author's experiments point to the fact that phenolsulphonic acid acts as a catalyst in the acetylation of cellulose, owing to the fact that free sulphuric acid is formed during the reaction. The addition of sodium phenolsulphonate to the mixture does not get rid of the free sulphuric acid, as the reaction between the sodium salt and sulphuric acid is slow. In commercial specimens of phenolsulphonic acid appreciable amounts of sulphuric acid are always present, but even when the pure sulphonic acid is used with pure acetic anhydride and cellulose, the presence of sulphuric acid can be detected after some little time. If barium phenolsulphonate is added to the mixture, the acetylation requires a much longer time, owing to the removal of

most of the sulphuric acid as insoluble barium sulphate. The addition of sulphates, for example, ferrous sulphate, dimethylamine sulphate, and sulphates derived from feeble bases, to acetic anhydride has also been recommended, and in these cases, also, the catalytic action is due to the liberation of small amounts of free sulphuric acid.

Various specimens of acetylcellulose have been prepared by Bayer's method (D.R.-P. 159524) and by Lederer's method (D.R.-P. 163316). The products have been hydrolysed by 25% aqueous potassium hydroxide solution at the ordinary temperature during forty-eight hours, and the reducing powers of the products of hydrolysis determined by means of boiling alkaline copper solution. After allowing for the reducing properties of the original cellulose and of the hydrated cellulose formed by the action of acids and alkalis on the cellulose (Normann, Abstr., 1906, i, 560), a mean copper value of four was obtained. This is due to the formation of hydrocelluloses, and the conclusion is drawn that the processes of Bayer and of Lederer are identical as regards their chemical mechanism. J. J. S.

Fixation of Bases by Soluble Starch. Eugène Fouard (*Bull. Soc. chim. Belg.*, 1910, 24, 105—109).—It is pointed out that there is no actual difference between the author's interpretation of his results (Abstr., 1909, i, 13, 209, 699) and that given by Reychler (Abstr., 1909, ii, 977). The action of bases appears to be to disintegrate the complex starch molecules with the formation of a simple group $(C_6H_{10}O_5)'$, which then reacts with the base, so that in the reversible reaction disintegration and re-formation of complex molecules occur. T. A. H.

Stachyose. Carl Neuberg and Siegbert Lachmann (*Biochem. Zeitsch.*, 1910, 24, 171—177).—Stachyose is only attacked very slowly by emulsin. It readily undergoes hydrolysis, however, when treated with yeast maltase and kephir lactase, yielding lævulose and mannino-triose. The last-named trisaccharide was obtained in the form of its osazone, which melts at 192—194°, and not at 122°, the melting point given by Tanret for the mannotrisacharideosazone prepared by him from stachyose. The authors also give their method of preparation of stachyose from the bulbs of *Stachys tubifera*. S. B. S.

New Compound Contained in Foods. A. Backe (*Compt. rend.*, 1910, 150, 540—543).—Baked bread and biscuits contain traces of a crystalline *compound*, m. p. 95°, which resembles in some respects Brandt's maltol, and shows many of the reactions of salicylic acid. It differs from the latter in its behaviour in Zipper's and Jorrisen's reactions, and in undergoing decomposition when heated with sodium hydroxide. With traces of ferric chloride, it develops a red coloration, becoming violet on adding a larger quantity of the reagent. The substance is isolated by treating bread with sulphuric or phosphoric acid, distilling in steam, and extracting the distillate with ether. It appears to be formed, together with maltol, when many sugars and starchy materials are acted on by an unknown enzyme and then heated at 120—150°. The enzyme necessary to its formation occurs together with amylase in flour and malt. W. O. W.

Preparation of Choline and Some of its Salts. Roemer R. Renshaw (*J. Amer. Chem. Soc.*, 1910, 32, 128—130).—Choline hydrochloride can be obtained in nearly quantitative yield by passing a current of dry trimethylamine into freshly distilled anhydrous ethylene chlorohydrin at $-12°$ to $-20°$ contained in a tube, which is afterwards sealed and heated for two hours at 80—90°. The salt can be purified by adding ether to an alcoholic solution. Choline *acetate*, *sulphate*, and *dihydrogen phosphate* are described. E. G.

Derivatives of Amino-acids. I. Compounds with Glycerol. Emil Abderhalden and Markus Guggenheim (*Zeitsch. physiol. Chem.*, 1910, 65, 53—60).—The authors have attempted to prepare derivatives of amino-acids with various aliphatic and aromatic compounds, including glycerol, in order to examine the behaviour of such compounds under the conditions which exist in the complete hydrolysis of proteins.

It has not been found possible to condense glycine or tyrosine with glycerol in the presence of dry hydrogen chloride at 185°, or glycerolsulphuric acid with glycine at 100°. Silver glycine and silver alanine do not react with the monohalohydrins of glycerol. Glycerolsulphuric acid, however, condenses with halogenated acyl chlorides.

Bisbromoisovalerylglycerol, $OH\cdot CH(CH_2\cdot O\cdot CO\cdot C_4H_9Br)_2$, obtained from bromo*iso*valeric acid, sulphuric acid, and glycerol at 70—80° (compare Grün, Abstr., 1905, i, 562; 1907, i, 462, 464), is a thin, colourless oil with a bitter taste, b. p. 185—200°/0·3 mm. Treatment with aqueous, alcoholic or liquid ammonia leads to decomposition of the ester and formation of a halogenated acid amide.

Glycine chloride does not appear to react with the sodium derivatives of glycerol, or yet with dipalmitin, in the presence of chloroform, but bromo*iso*valeryl bromide reacts with dipalmitin at 100°, yielding *glyceryl bromoisovalerate dipalmitate*,

$$C_{10}H_9Br\cdot CO\cdot O\cdot CH(CH_2\cdot O\cdot CO\cdot C_{15}H_{31})_2,$$

which crystallises in microscopic needles; it melts at 51° to a turbid liquid, which clarifies at 60°.

Tyrosine derivatives of glycerol are readily prepared, but are very sparingly soluble and difficult to purify.

Glycerolmonotyrosine,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

obtained by the action of glyceryl-α-monochlorohydrin on freshly prepared sodium tyrosinate, forms colourless needles, m. p. 245° (uncorr., decomp.), and is optically inactive. It is not hydrolysed when boiled for six hours with fuming hydrochloric acid. J. J. S.

Derivatives of Amino-acids. II. Compounds with Aliphatic Acids. Emil Abderhalden and Casimir Funk (*Zeitsch. physiol. Chem.*, 1910, 65, 61—68. Compare Bondi, Abstr., 1909, i, 458; Bondi and Frankl, *ibid.*, 459).—The authors object to the name lipopeptide for the condensation products of acyl chlorides with amino-acids; the name should be reserved for compounds containing a free amino-group.

Palmitylglycine, $CH_3\cdot[CH_2]_{14}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, obtained by the

action of palmityl chloride on glycine in the presence of dilute sodium hydroxide solution, crystallises in slender needles, m. p. 125° (corr.), after sintering at 119°. The corresponding *ethyl* ester, $C_{20}H_{39}O_3N$, also crystallises in needles, has m. p. 80—85°, and on hydrolysis yields palmitylglycine.

Palmityl-d-*alanine*, $CH_3\cdot[CH_2]_{14}\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, has m. p. 110°, after sintering at 105°, and $[\alpha]_D^{20}$ −5·98°.

Palmityl-l-*tyrosine*, $CH_3\cdot[CH_2]_{14}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH$, crystallises in plates, m. p. 133°, after sintering at 120°, and $[\alpha]_D^{20}$ +24·35°. *Palmityl*-l-*tyrosinyl palmitate*,

$$C_{15}H_{31}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot O\cdot CO\cdot C_{15}H_{31},$$

forms colourless needles, m. p. 95—96°, after sintering at 87°, $[\alpha]_D^{20}$ +15·28°.

Palmityl-3 : 5-*di-iodo*-l-*tyrosinyl palmitate*,

$$C_{15}H_{31}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_2I_2\cdot O\cdot CO\cdot C_{15}H_{31},$$

forms microscopic needles, sinters at 50°, melts at 55°, and forms a clear liquid at 62°.

Stearylglycine, $C_{17}H_{35}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, crystallises in plates, m. p. 155°, after sintering at 145°. *Stearyl*-d-*alanine*,

$$C_{17}H_{35}\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

crystallises in needles, m. p. 105—108°, $[\alpha]_D^{20}$ −4·55°.

Stearyl-l-*tyrosinyl stearate*,

$$C_{17}H_{35}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot O\cdot CO\cdot C_{17}H_{35},$$

forms slender needles, it sinters at 88°, melts at 98° to a turbid liquid, and becomes quite clear at 108°.

Palmityl-*dl*-phenylalanine, palmityl-*dl*-leucine, stearyl-*d*-glutamic acid, palmitylcystine, and palmityl-*l*-tryptophan have also been prepared.

It is difficult to obtain the tyrosine compounds in a state of purity.

J. J. S.

Synthesis of *dl*-Arginine (α-Amino-δ-guanino-*n*-valeric Acid) and of the Isomeric α-Guanino-δ-amino-*n*-valeric Acid. Sören P. L. Sörensen (*Ber.*, 1910, **43**, 643—651).—The proof that *d*-*l*-arginine is α-amino-δ-guanino-*n*-valeric acid has been established by condensing cyanamide with α-benzoylornithine to α-benzoylamino-δ-guanino-*n*-valeric acid and subsequent hydrolysis with hydrochloric acid, when a product identical with *d*-*l*-arginine is obtained.

The isomeric δ-amino-α-guanino-*n*-valeric acid can by obtained in a similar manner from δ-benzoylornithine.

A 75% yield of δ-benzoylornithine is obtained when ornithuric acid is boiled with hydrochloric acid, and a 52% yield of the isomeric *α-benzoylornithine*, $NH_2\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot COPh$, is obtained when ornithuric acid is boiled with barium hydroxide solution. The α-compound forms long, thin crystals, m. p. 264—267°, is some three to four times as soluble in water as the δ-compound, and does not crystallise so readily. The δ-compound (Fischer, *Ber.*, 1901, **34**, 463) has m. p. 285—288°. The constitution of the two benzoyl derivatives has been established by replacing the amino-groups by hydroxyl. α-Benzoylamino-δ-hydroxyvaleric acid (Abstr., 1908, i, 651) has m. p. 160° (not 170°). The *δ-benzoylamino-α-hydroxyvaleric acid*,

$$C_6H_5\cdot CO\cdot NH\cdot[CH_2]_3\cdot CH(OH)\cdot CO_2H,$$

is readily soluble in water, crystallises from benzene in needles, m. p. 85°, yields a sparingly soluble *barium* salt, and when hydrolysed yields Fischer and Zemplen's δ-amino-α-hydroxyvaleric acid (this vol., i, 100).

*α-Benzoylamino-δ-guanino-*n*-valeric acid*,

$$NH_2\cdot C(:NH)\cdot NH\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot COPh,$$

obtained, together with dicyanodiamide and barium carbonate, by leaving α-benzoylornithine and cyanamide in contact with 0·4*N*-barium hydroxide solution for a month, crystallises in well developed four- and six-sided plates, and also in stout prisms, m. p. 315° (decomp.).

*δ-Benzoylamino-α-guanino-*n*-valeric acid*,

$$COPh\cdot NH\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot C(:NH)\cdot NH_2,$$

obtained in a similar manner from δ-benzoylornithine, forms a curdy mass of minute needles containing $3H_2O$. When anhydrous it has m. p. 175—180°. J. J. S.

Synthesis of Glycylaminoacetaldehyde. Carl D. Harries and Irnfried Petersen (*Ber.*, 1910, **43**, 634—639).—Polypeptides obtained from amino-acids and amino-aldehydes are termed *peptals*, the simplest representative being *glycylaminoacetaldehyde*,

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CHO.$$

This aldehyde has been synthesised by the two following methods: 1. Glycylallylamine, obtained by the action of ammonia on the condensation product of allylamine and chloroacetyl chloride, is readily oxidised in the form of its hydrochloride to glycylaminoacetaldehyde by means of ozone (compare Harries and Richard, Abstr., 1904, i, 295). 2. Glycylaminoacetal, obtained by the action of ammonia on the condensation product of chloroacetyl chloride and aminoacetal, is hydrolysed by hydrochloric acid to glycylaminoacetaldehyde.

The aldehyde has so far not been obtained pure, but merely in the form of a syrup with strongly reducing properties.

Chloroacetylallylamine, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CH{:}CH_2$, is a colourless, syrupy liquid, b. p. 110—112°/14 mm., and solidifies in a freezing mixture; it has $D^{19\cdot5}_{19\cdot5}$ 1·1683 and $n_D^{19\cdot5}$ 1·48917. *Glycylallylamine*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH{:}CH_2$, is a colourless oil, b. p. 85—91°/0·19 mm., D^{20}_{20} 1·0532, and n_D^{20} 1·49585. It absorbs carbon dioxide rapidly, and forms a *picrate*, $C_{11}H_{13}O_8N_5$, m. p. 136—138°. The *benzoyl* derivative, $C_{12}H_{14}O_2N_2$, crystallises in plates, m. p. 138°. If liquid ammonia is used instead of an aqueous solution for replacing the chlorine in chloroacetylallylamine, a by-product is obtained, which has b. p. 187°/0·19 mm.; it is probably *iminodiacetyldiallylamine*,

$$NH(CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH{:}CH_2)_2.$$

Chloroacetylaminoacetal, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, has b. p. 80—85°/0·14 mm., and solidifies to a colourless, crystalline mass, m. p. 29—30°.

Glycylaminoacetal, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, has b. p. 107—110°/0·14 mm. and m. p. 42—45°, and yields a colourless, crystalline hydrochloride, $C_8H_{18}O_3N_2,HCl$. The acetal is readily hydrolysed by cold dilute hydrochloric acid. J. J. S.

Preparation of Nitrogen Derivatives of Formaldehydesulphoxylic Acid. Chemische Fabrik von Friedr. Heyden (D.R.-P. 216074).—The reduction of *sodium aminomethylsulphite*,

$$NH_2(CH_2{\cdot}O{\cdot}SO_2Na),$$

sodium iminodimethylsulphite, $NH(CH_2{\cdot}O{\cdot}SO_2Na)_2$, and of sodium nitrilotrimethylsulphite, $N(CH_2{\cdot}O{\cdot}SO_2Na)_3$, with zinc at 60—70° in either acid or ammonium hydroxide solution yields respectively *sodium aminomethylsulphoxylate*, $NH_2(CH_2{\cdot}O{\cdot}SONa)$, *sodium iminodimethylsulphoxylate*, $NH(CH_2{\cdot}O{\cdot}SONa)_2$, and *sodium nitrilotrimethylsulphoxylate*, $N(CH_2{\cdot}O{\cdot}SONa)_3$.

The relative proportion of indigotin reduced by these substances is stated in the patent. F. M. G. M.

Preparation of Nitrogen Derivatives of Aldehyde Bisulphites. Chemische Fabrik von Friedr. Heyden (D.R.-P. 216072).—*Sodium iminodimethylsulphite*, $NH(CH_2{\cdot}O{\cdot}SO_2Na)_2$, is prepared by treating a solution of ammonium hydroxide with two molecular proportions of formaldehyde bisulphite solution at 45° and evaporating under reduced pressure, when the product separates as a colourless powder, or as hard crystals. The ammonium hydroxide in the foregoing reaction can be replaced by other primary amines, the resulting products being powerful reducing agents. F. M. G. M.

Preparation of Nitrogen Derivatives of Aldehyde Bisulphites. Chemische Fabrik von Friedr. Heyden (D.R.-P. 216073. Compare preceding abstract).—*Sodium nitrilotrimethylsulphite*,

$$N(CH_2{\cdot}O{\cdot}SO_2Na)_3,3H_2O,$$

separates as prismatic crystals when a solution containing three molecular proportions of formaldehyde bisulphite and one of ammonia is concentrated under reduced pressure ; it is readily soluble in water, sparingly so in alcohol, is decomposed by sodium hydroxide with evolution of ammonia, and by mineral acids with elimination of sulphurous acid. F. M. G. M.

Preparation of Nitrogen Derivatives of Formaldehydesulphoxylates. Chemische Fabrik von Friedr. Heyden (D.R.-P. 216121).—*Sodium nitrilotrimethylsulphoxylate*, $N(CH_2{\cdot}O{\cdot}SONa)_3$, can be prepared by reducing sodium nitrilotrimethylsulphite,

$$N(CH_2{\cdot}O{\cdot}SO_2Na)_3,$$

with zinc in either acid or ammonium hydroxide solution, and subsequently concentrating in a vacuum ; it is a colourless, resinous mass, very readily soluble in water, insoluble in anhydrous solvents, and reduces indigo-carmine rapidly in the cold. The *zinc* salt is a powerful reducing agent ; the *calcium* salt is somewhat sparingly soluble in sodium chloride solution. F. M. G. M.

ζ-Amino-ketones. II. Siegmund Gabriel (*Ber.*, 1910, 43, 356—362. Compare Abstr., 1909, i, 891).—Methyl ζ-aminohexyl ketone, the *benzenesulphonyl* derivative of which has m. p. 77—78°, is reduced by sodium and alcohol to η-hydroxyoctylamine, which forms a *hydrochloride*, $OH{\cdot}CHMe{\cdot}[CH_2]_6{\cdot}NH_2,HCl$, m. p. above 80°, a *platinichloride*, m. p. 201° (decomp.), and is converted by concentrated hydrochloric acid at 100° into *η-chloro-octylamine*, which forms a

platinichloride, darkening at 206°, and decomposing at 210°. A by-product of the reduction is a *substance*, $C_8H_{17}N$, which appears to be a saturated secondary base, and is possibly 2-methylheptamethyleneimine; it forms a *hydrochloride*, m. p. 148—149°, *platinichloride*, m. p. 153—155°, *aurichloride*, m. p. 67—68°, *picrate*, m. p. 152—153°, and a *benzenesulphonyl* derivative, $C_8H_{16}N\cdot SO_2Ph$, m. p. 114—115°, which is insoluble in alkalis. C. S.

Partial Inversion of Optical Antipodes. Oscar Lutz (*Zeitsch. physikal. Chem.*, 1910, 70, 256—262).—In the course of his investigations on the Walden inversion, Fischer (compare Fischer and Raske, Abstr., 1907, i, 381) has shown that the occurrence of inversion depends on the nature of the substance acted on as well as on that of the reagent. The author has already shown (compare Abstr., 1908, i, 345) that by the action of dibenzylamine on *l*-bromosuccinic acid both a malamic acid and an aspartic acid are produced; the former action proceeds normally, the latter abnormally. It is now shown that a similar partial inversion occurs when methylamine acts on *l*-bromosuccinic acid.

The reacting substances were brought together in a mixture of methyl alcohol and water; the mixture was kept for a week at the ordinary temperature, and was then heated on the water-bath. The products, *d*-β-methylmalamic acid and *l*-methylaspartic acid, were separated by fractional crystallisation of the silver salts. The former acid has $[\alpha]_D$ +13·0°. The latter acid crystallises with $1H_2O$, melts at 183—184°, and forms a salt with one molecule of hydrogen chloride. Its optical behaviour does not correspond with that of aspartic acid. In aqueous solution, methylaspartic acid, in the presence of varying proportions of hydrochloric acid, gave values of $[\alpha]_D$ between −22·6° and −30·8°; in the presence of alkali (5 c.c. of *N*/1-sodium hydroxide added to 0·1105 gram of the anhydrous salt and the solution made up to 20 c.c.), $[\alpha]_D$ −29·8°. As this acid has not so far been brought into simple relationship with the optically active malic acids, its configuration is not regarded as being conclusively established. G. S.

Glutamic Acid and Pyrrolidinecarboxylic Acid. Emil Abderhalden and Karl Kautzsch (*Zeitsch. physiol. Chem.*, 1910, 64, 447—459).—As a preliminary to a study of the importance of these substances in metabolism, especially in hæmoglobin formation, a number of salts were prepared and their properties investigated. Monobasic *sodium glutamate*, $C_5H_8O_4NNa$: a crystalline, hygroscopic salt containing 2% water of crystallisation, m. p. 160—170°. Monobasic *calcium glutamate*, $(C_5H_8O_4N)_2Ca$: amorphous. Monobasic *barium glutamate*: hygroscopic, crystallisable from dilute alcohol. Dibasic *copper glutamate*, $C_5H_7O_4NCu,\frac{1}{4}H_2O$: amorphous, greenish-blue. *Potassium glutamate*, $C_5H_8O_4NK$. Monobasic *lead glutamate*, $(C_5H_8O_4N)_2Pb$: hygroscopic.

Attempts were also made to prepare iron salts, but with indifferent results.

Pyrrolidinecarboxylic acid was prepared by heating glutamic acid at 180—190°. It has m. p. 182—184° (corr.), $[\alpha]_D^{20}$ +7·29°. After

treatment with hydrochloric acid gas, a crystalline substance was obtained with the m. p. of glutamic acid hydrochloride. The *calcium* salt, $(C_5H_6O_3N)_2Ca$, was prepared; it is crystalline and hygroscopic. The monobasic *calcium aspartate*, $(C_4H_4O_5N)_2Ca$, and the dibasic *copper aspartate* were also prepared. W. D. H.

Decomposition of Metallic Cyanates by Water. Orme Masson and Irvine Masson (*Zeitsch. physikal. Chem.*, 1910, 70, 290—314).—The rate of decomposition of the metallic cyanates by water was followed by estimating both the carbonate and unaltered cyanate after heating for definite intervals. The carbonate, if not already precipitated in the course of the reaction, was thrown down by excess of barium nitrate, the precipitate washed, and estimated volumetrically. The cyanate remaining in solution was precipitated by a known excess of silver nitrate, washed, and the unprecipitated silver determined by Volhard's method. All the measurements were made at 80°.

The cyanates of metals forming insoluble carbonates (for example, barium and calcium) are decomposed by water in accordance with the equation: $M(CNO)_2 + 2H_2O = MCO_3 + CO(NH_2)_2$. The change consists of two consecutive reactions: (1) a slow reaction representing the hydrolysis of CNO′ ions, which immediately yield insoluble carbonate and $NH_4^{\cdot}$ ions; (2) the reaction of the $NH_4^{\cdot}$ ions with CNO′ ions to form carbamide. As the second action is relatively rapid, the $NH_4^{\cdot}$ ions are kept at a very small constant concentration. No appreciable effect is produced by the reverse decomposition of carbamide, even if some excess of the latter is added at the outset.

The cyanates of sodium and potassium are decomposed by water according to the equation:

$$4MCNO + 6H_2O = 2M_2CO_3 + (NH_4)_2CO_3 + CO(NH_2)_2,$$

and the ratio of the products thus indicated persists for the whole course of the reaction after a short initial stage. The products of the reaction, more particularly the ammonium carbonate, accelerate the reaction, and if initially added in proportions other than that in which they are produced in the reaction, they alter the relative proportion of the products. Excess of ammonium carbonate tends to increase the carbamide formation relatively to that of ammonium carbonate, whilst excess of metallic carbonate has the converse effect, so that the action is automatically regulated in the direction of the normal ratio. G. S.

Fulminic Acid. Lothar Wöhler (*Ber.*, 1910, 43, 754—756).—Polemical against the historical accuracy of a monograph by Wieland on fulminic acid (*Ahrensche Sammlung*, Vol. XIV, Nos. 11 and 12). T. S. P.

Dicyanodiamidine Compounds. Hermann Grossmann and B. Schück (*Ber.*, 1910, 43, 674—676. Compare Söll and Stutzer, this vol., i, 14).—Commercial dicyanodiamidine sulphate contains no other organic compound as impurity, and may be used for the quantitative estimation of nickel.

Dicyanodiamidinium platinichloride, $(C_2H_6ON_4)_2PtCl_6$, is a yellow, crystalline substance.

Palladiumdicyanodiamidine, $Pd(C_2H_5ON_4)_2,2H_2O$, is obtained as a yellow, crystalline, almost insoluble precipitate on mixing dicyanodiamidine sulphate with palladium chloride and potassium hydroxide. It is soluble in ammonia. E. F. A.

Molybdenum Cyanides. Arthur Rosenheim (*Zeitsch. anorg. Chem.*, 1910, 66, 95—96).—The doubled formula suggested by Rosenheim, Garfunkel, and Kohn (this vol., i, 101) for potassium molybdenum cyanide must be abandoned. Miolati points out that $Mo_2^{V}(CN)_8$ requires just as much oxygen to convert it into molybdic acid as $2Mo^{IV}(CN)_4$, as $Mo_2^{V}(OH)_8$ must first be converted into $Mo_2^{VI}(OH)_{10}$ or $2Mo^{V}(OH)_5$, and then into $2Mo^{VI}(OH)_6$. R. Weinland suggests the formula $K_4Mo^{V}(OH)(CN)_8aq.$, which is possibly correct. C. H. D.

Aliphatic Diazo-salts. Karl A. Hofmann and Rudolf Roth (*Ber.*, 1910, 43, 682—688. Compare Abstr., 1906, i, 907).—Aminoguanidine dinitrate when diazotised in aqueous solution at 0° with sodium nitrite forms *aminoguanidine diazohydroxide*, $C_2H_7N_{10}\cdot OH$. This is obtained as a colourless, crystalline powder, composed of microscopic, transparent, pointed prisms. It explodes when struck or when heated at 135—140°. It behaves as a diazo-compound; when boiled with water, 3 atoms of nitrogen are eliminated; 15% sulphuric acid liberates 2 atoms. A fourth nitrogen atom is concerned in the formation of aminotetrazolic acid when the diazohydroxide is boiled with water. The diazohydroxide does not form a hydrazine, and yields 4 molecules of ammonia when evaporated with concentrated potassium hydroxide, showing that the amino- and imino-groups of the aminoguanidine molecule remain intact.

The *chloride*, $C_2H_7N_{10}\cdot Cl$, is obtained in colourless, silky, lustrous prisms or needles, and explodes at 140°. When boiled in water, between 3 and 4 atoms of nitrogen are liberated. Water eliminates hydrogen chloride, indicating that the salt is not of the basic type of the aromatic diazonium salts, but belongs to the group of the diazhydroxides, $N{:}N\cdot OH$. The chloride couples slowly with aromatic amines; α-naphthylamine shows a deep red solution; β-naphthylamine and *m*-phenylenediamine give a brownish-red-yellow coloration. Both hydroxide and chloride when heated with resorcinol and sulphuric acid show an intense violet coloration, which becomes red with a red fluorescence on the addition of excess of ammonia.

The *perchlorate* forms colourless, clear prisms of very explosive nature. It is completely hydrolysed by cold water.

The *nitrate* crystallises in minute, doubly refractive needles; it is less easily exploded.

The *sulphate* is a fine, colourless powder.

The diazohydroxide also combines with bases; with sodium hydroxide it forms an almost colourless solution. After evaporation on the water-bath and the addition of acid, the product can still be coupled. Excess

of silver nitrate causes a precipitate; from the ammoniacal solution the *silver* salt separates in lustrous, centrically-arranged, snow-like crystals, which are very explosive. A *copper* salt is more stable.

E. F. A.

Preparation and Decomposition of the Oximino-derivative of Ethyl Malonylbishydrazoneacetoacetate. Carl Bülow and Carl Bozenhardt (*Ber.*, 1910, **43**, 551—563. Compare Abstr., 1908, i, 253; this vol., i, 102).—When ethyl malonylbishydrazoneacetoacetate reacts with nitrous acid, only two of the three reactive methylene groups take part, namely, the two terminal groups, and the product obtained is the dioximino-derivative,

$$CH_2[CO\cdot NH\cdot N{:}CMe\cdot C(CO_2Et){:}N\cdot OH]_2.$$

A better yield of the same compound can be obtained by the condensation of V. Meyer's ethyl oximinoacetoacetate (Abstr., 1878, 487) with malonyldihydrazide.

When an excess of nitrous gases is led into a chloroform solution of ethyl malonylbishydrazoneacetoacetate, a molecule of ethyl oximinoacetoacetate is eliminated, and the bisoximino-derivative of malonylhydrazoneacetoacetic acid,

$$OH\cdot N{:}C(CO_2H)\cdot CMe{:}N\cdot NH\cdot CO\cdot C(CO_2H){:}N\cdot OH,$$

is formed according to the equation:

$$CH_2[CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et]_2 + 3HNO_2 =$$
$$EtOH + N_2H_4 + COMe\cdot C(:N\cdot OH)\cdot CO_2Et +$$
$$OH\cdot N{:}C(CO_2H)\cdot CMe{:}N\cdot NH\cdot CO\cdot C(CO_2H){:}N\cdot OH.$$

Ethyl oximinomalonylbishydrazoneoximinoacetoacetate,

$$CH_2[CO\cdot NH\cdot N{:}CMe\cdot C(:N\cdot OH)\cdot CO_2Et]_2,$$

crystallises in needles with a nacreous lustre, and has m. p. 200—201°. When boiled for some sixty hours with pure alcohol, it yields malonic acid and the hydrazone of ethyl oximinoacetoacetate, which is immediately transformed into 4-oximino-3-methyl-5-pyrazolone (compare Knorr, Abstr., 1903, i, 660; Betti, Abstr., 1904, i, 533; Wolff, *ibid.*, 722; Bülow and Schaub, Abstr., 1908, i, 687). The same decomposition can be effected by sulphuric acid, sodium hydroxide solution, or ammonium hydroxide, whereas phenylhydrazine reacts with it, yielding hydroxylamine, malonic acid, and 4-*anilinoazo*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, $C_{16}H_{14}ON_4$, m. p. 154—155°.

Attempts have been made to synthesise ethyl oximinomalonylhydrazoneoximinoacetate from *malonamidehydrazide*,

$$NH_2\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

which can be obtained by the action of hydrazine hydrate on an alcoholic solution of ethyl malonamate (Pinner and Oppenheimer, *Ber.*, 1895, **28**, 478). The hydrazide crystallises in glistening needles, resembling urea, and has m. p. 126—127°. Ethyl acetoacetate condenses with the hydrazide at 40° in the presence of a few drops of water, yielding *ethyl malonamidehydrazoneacetoacetate*,

$$NH_2\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et,$$

which crystallises in colourless, felted needles, m. p. 118·5°. It decomposes at 160°, solidifies again at 162°, and then melts at 190—192° to a yellow liquid. It reacts with nitrous acid, yielding

ethyl oximinoacetoacetate according to the equation :

$$NH_2\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et + 5HNO_2 = COMe\cdot C(:NOH)\cdot CO_2Et + 5N + NO + 5H_2O + 2CO_2 + HCN.$$

J. J. S.

Amphoteric Nature of Cacodylic Acid. Bror Holmberg (*Zeitsch. physikal. Chem.*, 1910, 70, 153—157).—Hantzsch and others regard cacodylic acid as an ordinary weak acid, whilst Johnston (Abstr., 1904, i, 984) has brought forward evidence to show that it is an amphoteric electrolyte. In order to settle the question, the author has determined the $H^{\cdot}$-ion concentration by the diazoacetic ester method in mixtures of the acid with picric acid and nitric acid respectively, and also in aqueous solutions of the acid itself. The results confirm the view of Johnston that cacodylic acid is an amphoteric electrolyte; the value of k_a is about $7{\cdot}5 \times 10^{-7}$, and that of k_b about $5{\cdot}6 \times 10^{-13}$ at 25°. G. S.

New Method of Bromination. Bromination with Aqueous Hypobromous Acid. Otto Stark (*Ber.*, 1910, 43, 670—674).—The use of hypobromous acid, prepared by digesting bromine and water with excess of powdered mercuric oxide, in the form of a straw-yellow solution containing about 6·2% of bromine, is suggested as a brominating agent. It suffices to shake this in the cold with benzene, toluene, or benzoic acid to obtain satisfactory yields of monobromobenzene, *o*- and *p*-bromotoluene, and *m*-bromobenzoic acid. Aniline yields tribromoaniline; phenol gives tribromophenol under similar conditions; nitrobenzene resists bromination, as also does phthalic acid.

E. F. A.

Compounds of Aluminium Chloride with Nitro-compounds of Benzene Hydrocarbons and their Derivatives. Boris N. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 58—94).—The author has investigated the freezing-point diagrams of the systems formed by aluminium chloride with nitrobenzene, and with each of the three chloronitrobenzenes, bromonitrobenzenes, and nitrotoluenes. The m.p.'s of the compounds formed, the two eutectic points, and the compositions corresponding with them are compared with the corresponding data for the systems with aluminium chloride (Abstr., 1909, i, 900).

Nitrobenzene forms the two compounds: (1) $AlCl_3,C_6H_5\cdot NO_2$; and (2) $AlCl_3,2C_6H_5\cdot NO_2$, which crystallises in almost colourless, hygroscopic, rhombic plates, m. p. 25·5° (decomp.).

o-, *m*-, and *p*-Chloronitrobenzenes form compounds of the type $AlCl_3,C_6H_4Cl\cdot NO_2$, having m. p.'s 89°, 104°, and 126° respectively. With the bromonitrobenzenes, compounds of the type

$$AlCl_3,C_6H_4Br\cdot NO_2$$

are formed, the m. p.'s being 100°, 116°, and 145° respectively for the *o*-, *m*-, and *p*-derivatives.

o- and *m*-Nitrotoluenes form compounds of the two types: (1) $AlCl_3,C_6H_4Me\cdot NO_2$, both of which have m. p. 99·5°, and (2) $AlCl_3,2C_6H_4Me\cdot NO_2$, decomposing at 55·1° and 35° respectively. *p*-Nitrotoluene gives only the compound $AlCl_3,C_6H_4Me\cdot NO_2$, m.p. 109°.

Excepting in the case of *m*-bromonitrobenzene, the compounds with aluminium chloride melt at higher temperatures than the corresponding compounds formed by the bromide. The first eutectic points and the compositions at these points differ only slightly for the two series of compounds; in the case of the meta-derivatives, the eutectic mixture always contains a larger proportion of the organic compound than with the corresponding ortho- or para-derivatives.

The temperatures of the second eutectic points are considerably higher for the aluminium chloride than for the bromide systems, although the m. p.'s of the two series of compounds exhibit only small differences. The proportions of organic compound to 1 mol. of aluminium chloride (or bromide) at the second eutectic point vary only slightly, the mean value being 0·653 (or 0·484) mol.

The stability of the aluminium chloride systems is, in general, greater than that of the corresponding aluminium bromide systems, but the solubility curves exhibit similar forms in the two cases.

T. H. P.

The Real State of Metastyrene and the Polymerisation of Styrene by Light and Heat. Hans Stobbe and Georg Posnjak (*Annalen*, 1910, **371**, 259—286).—This investigation was undertaken owing to the contradictory nature of the statements of many investigators who have worked on this subject (compare Blyth and Hofmann, *Annalen*, 1845, **53**, 289; Berthelot, *Bull. Soc. chim.*, 1866, [ii], **6**, 294; Krakau, *Ber.*, 1878, **11**, 1260; Lemoine, Abstr., 1898, i, 70; 1900, i, 91; Kronstein, Abstr., 1903, i, 80).

Metastyrene is formed by the action of light or heat on styrene, and is obtained as a white, odourless, amorphous substance by adding alcohol to a solution of the compound in benzene; it does not produce an elevation of the b. p. of a solvent, and is consequently to be regarded as a colloid. The substances described hitherto as metastyrene are mixtures of this substance and styrene; thus, the gelatinous variety is composed of equal parts of these substances, whilst the vitreous modification contains about 20% of styrene.

Metastyrene is quite indifferent towards bromine and potassium permanganate, and is undoubtedly a polymerisation product of styrene, since it passes almost quantitatively into this hydrocarbon at about 320°.

The velocity with which styrene changes into metastyrene under the influence of light and heat has been ascertained by comparison of the viscosity of the substance under observation with that of mixtures of the two substances having a known composition. It is found that (1) the velocity of polymerisation increases with the time; (2) the reaction proceeds in the dark and without the application of heat after it has been started by the action of light, and (3) freshly distilled styrene, under identical conditions, does not polymerise so rapidly as a sample which has been kept in the dark for several days after distillation.

W. H. G.

Liquid and Solid Distyrene. Hans Stobbe and Georg Posnjak (*Annalen*, 1910, **371**, 287—302).—Liquid distyrene, which results

from the action of hydrobromic acid or 50% sulphuric acid on cinnamic acid (compare Erlenmeyer, *Annalen*, 1865, **135**, 122; Erdmann, Abstr., 1883, 474), is shown to be $a\gamma$-diphenyl-Δ^{α}-butene, whilst the crystalline distyrene obtained by the destructive distillation of calcium cinnamate (Engler and Leist, Abstr., 1873, 901) and β-truxillic acid (Liebermann, Abstr., 1889, 1194) is $a\delta$-diphenyl-Δ^{α}-butene. Both hydrocarbons yield benzaldehyde when oxidised with chromic acid; the absorption spectra have also been measured, and are represented graphically.

$a\gamma$-Diphenyl-Δ^{α}-butene combines with bromine, forming $a\beta$-dibromo-$a\gamma$-diphenylbutane, m. p. 102° (compare Erdmann, *loc. cit.*), and, when reduced with hydriodic acid and red phosphorus yields, *$a\gamma$-diphenylbutane*, $CH_2Ph{\cdot}CH_2{\cdot}CHMePh$, a pale yellow oil, b. p. 295°.

$a\beta$-Dibromo-$a\delta$-diphenylbutane, m. p. 238° (compare Liebermann, *loc. cit.*), when reduced with alcohol and sodium amalgam, yields $a\delta$-diphenylbutane (compare Freund and Immerwahr, Abstr., 1890, 1407).

$\beta\gamma$-Dibromo-$\beta\gamma$-diphenylbutane, $CMePhBr{\cdot}CMePhBr$, was prepared for the purpose of comparison by treating acetophenonepinacone with acetyl bromide and subsequently with phosphorus pentabromide; it crystallises in small, slender, silky needles, m. p. 140—145° (decomp.).

W. H. G.

Triarylmethyls. II. Triphenylmethyl and Analogues of Triphenylmethyl in the Diphenyl Series. Wilhelm Schlenk, Tobias Weickel, and Anna Herzenstein (*Annalen*, 1910, **372**, 1—20. Compare Abstr., 1909, i, 791).—*Tridiphenylmethyl* (*4 : 4′ : 4″-triphenyltriphenylmethyl*), $C(C_6H_4Ph)_3$, has been prepared by the action of copper bronze (*Naturkupfer* C) on a solution of 4 : 4′ : 4″-triphenyltriphenylmethyl chloride in benzene; it is a dark green, crystalline powder, m. p. 186° (in a sealed tube), solutions of which in organic solvents are deep violet, although thin layers are green. Unlike triphenylmethyl, solutions which have been decolorised by shaking with a small quantity of oxygen do not become coloured when kept; this is due to the fact that, from mol.-wt. determinations, tridiphenylmethyl is present in solution only in the unimolecular, coloured modification. Tridiphenylmethyl combines readily with oxygen, yielding the *peroxide*, $C_{74}H_{54}O_2$, a white, crystalline powder, m. p. 198°.

4-Phenyltriphenylmethyl and *4 : 4′-diphenyltriphenylmethyl* have been prepared by the same method, but do not crystallise readily. The solution of the former in benzene is orange-red; it is decolorised by shaking with a small quantity of oxygen, the *peroxide*, $C_{50}H_{38}O_2$, m. p. 180°, being formed; as in the case of triphenylmethyl, the colour returns when the solution is kept for a short time. The solution of 4 : 4′-diphenyltriphenylmethyl in benzene is red, and likewise contains the coloured and colourless modifications in a state of equilibrium, but in this case the proportion of the latter is very small.

4-Phenyltriphenylmethyl is converted by hydrogen chloride in benzene into 4-phenyltriphenylmethane and 4-phenyltriphenylmethyl chloride, and in this respect differs from triphenylmethyl, which, under similar treatment, has been shown to yield benzhydryltetra-

phenylmethane; it is found, however, that small quantities of triphenylmethane and triphenylmethyl chloride are also formed from triphenylmethyl.

Solutions of 4-phenyltriphenylmethyl chloride, 4 : 4′-diphenyltriphenylmethyl chloride, and 4 : 4′ : 4″-triphenyltriphenylmethyl chloride in liquid sulphur dioxide are orange-red, red, and violet respectively; the unaltered substances are obtained when the sulphur dioxide is allowed to evaporate, except in the last case, when the *additive* product, $(C_6H_4Ph)_3CCl,4SO_2$, is obtained in magenta-like crystals having an intense metallic lustre; a similar *additive* compound is obtained with tridiphenylmethyl. It follows from these observations that the liquid sulphur dioxide does not function merely as a solvent, and, consequently, the assumption that the electrical conductivity of solutions of triphenylmethyl in sulphur dioxide is due to negative and positive triphenylmethyl ions (compare Gomberg, Abstr., 1907, i, 504) is very improbable. It is shown, however, that triphenylmethyl chloride and bromide are dissociated in liquid sulphur dioxide, for it has been found possible to obtain a solution of triphenylmethyl in the cathode chamber by electrolysing these solutions.

The mono-, di-, and tri-phenyl derivatives of triphenylmethyl chloride, in analogy to the alkali halides, turn yellow, orange-red, and violet respectively under the influence of ultraviolet light, probably owing to dissociation into triarylmethyl and halogen; the colour disappears when the substance is subsequently exposed to ordinary light for some time.

The bearing of the observations recorded in the paper on the question of the constitution of triphenylmethyl is discussed; the conclusion is drawn that the constitution of this substance is most suitably represented, not by a quinonoid structural formula, but by the simple formula CPh_3, in which the carbon is tervalent; the unimolecular triarylmethyls are electrically neutral molecules and not ions, for solutions of tridiphenylmethyl in benzene do not conduct.

4-*Phenyltriphenylmethane*, $CHPh_2{\cdot}C_6H_4Ph$, prepared by reducing the corresponding carbinol with glacial acetic acid and zinc dust, crystallises in long needles, m. p. 112—113°. 4 : 4′-*Diphenyltriphenylmethane*, $CHPh(\cdot C_6H_4Ph)_2$, crystallises with $1C_6H_6$ in leaflets, m. p. 161°. W. H. G.

Triarylmethyls. III. Diphenyldiphenylenecarbinol. Wilhelm Schlenk and Anna Herzenstein (*Annalen*, 1910, **372**, 21—31. Compare preceding abstract).—In the preceding paper, tridiphenylmethyl is shown to differ from other triarylmethyls in that it exists wholely in solution in the unimolecular state; an attempt to obtain a "triarylmethyl" of an opposite character, namely, one which in solution exists only in the bimolecular state, has been successful.

In the preparation of 4 : 4′ : 4″-triphenyltriphenylcarbinol (compare Abstr., 1909, i, 791), a substance was obtained which examination has shown to be diphenyldiphenylenecarbinol (4-phenylphenyldiphenylenecarbinol); this substance, when treated with acetyl chloride, yields the corresponding chloride, which differs from the analogous triarylmethyl chlorides examined hitherto in that the solutions in

phenol and liquid sulphur dioxide are colourless; further, the solution in benzene when treated with metals remains colourless, the product formed being $\alpha\beta$-bisdiphenyl-$\alpha\beta$-bisdiphenylene-ethane. The latter substance differs from hexaphenylethane (triphenylmethyl) and other triarylmethyls, not only in existing in solutions in an undissociated state, but also in not combining readily with oxygen; a peroxide is formed, however, by passing oxygen into the solution during the action of copper on the chloride. The fact that $\alpha\beta$-bisdiphenyl-$\alpha\beta$-bisdiphenylene-ethane does not dissociate in solution, shows that the valency acting between the two substituted methyl groups represents a much greater affinity than in the other hexa-arylethanes which have been investigated. In complete agreement with this, diphenyldiphenylenemethyl chloride does not so readily form additive products as other triarylmethyl chlorides (compare Werner, Abstr., 1906, i, 436); thus, tridiphenylmethyl is completely dissociated in benzene, and tridiphenylmethyl chloride forms a moderately stable additive compound with sulphur dioxide (compare preceding abstract); 4-phenyltriphenylmethyl and 4 : 4′-diphenyltriphenylmethyl are partly dissociated in benzene, whilst additive compounds of the chlorides with sulphur dioxide exist, but are unstable; diphenyldiphenylenemethyl chloride does not form an additive product with sulphur dioxide.

Diphenyldiphenylenemethyl chloride, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!CCl\cdot C_6H_4Ph$, is most readily prepared by the action of 9 : 9-dichlorofluorene on a solution of diphenyl in carbon disulphide in the presence of aluminium chloride; it crystallises in coarse granules, m. p. 138—140°, and forms intensely coloured, double *salts* with stannic chloride and aluminium chloride; when treated with hot glacial acetic acid and sodium acetate, it yields *diphenyldiphenylenecarbinol*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C(OH)\cdot C_6H_4Ph$, which crystallises from benzene-light petroleum in stellate groups of slender needles, m. p. 137—139°, and by precipitation from glacial acetic acid in four-sided leaflets, m. p. 149°; the latter compound forms (1) an *additive* compound with fluorenone, crystallising in pale yellow octahedra, m. p. 123°; (2) a *perchlorate*, crystallising in deep blue prisms with a metallic reflex; (3) an *ethyl ether*, m. p. 167°.

$\alpha\beta$-Bisdiphenyl-$\alpha\beta$-bisdiphenylene-ethane,

$$C_6H_4Ph\cdot C(:C_{12}H_8)\cdot C(:C_{12}H_8)\cdot C_6H_4Ph,$$

forms small, colourless prisms, m. p. 175—176°; the *peroxide*, $C_{50}H_{34}O_2$, forms six-sided leaflets, m. p. 193°. W. H. G.

Formation of Colourless Ions from Triphenylmethyl Bromide. Arthur Hantzsch and Kurt H. Meyer (*Ber.*, 1910, 43, 336—340).—Triphenylmethyl bromide forms a colourless, electrically conducting solution in pyridine and in acetone; its conducting solution in acetonitrile is yellow at the ordinary temperature, colourless at 0°. Its conductivity in pyridine diminishes rapidly with time, attaining after about one hour a constant value, about half the initial value, and identical with that of *triphenylmethylpyridinium bromide*, $CPh_3\cdot C_5NH_5Br$, a colourless, crystalline substance obtained by the

addition of pyridine to a benzene solution of triphenylmethyl bromide. The change of conductivity is attributed to the conversion of the bromide, which functions initially as a carbonium salt by the addition of pyridine, into an ammonium salt. Triphenylmethyl chloride exhibits a converse behaviour in pyridine, the conductivity slowly increasing with time.

Tri-α-phenyldi-β-methylpropane, $CPh_3 \cdot CMe_3$, m. p. 185°, is obtained from magnesium *tert.*-butyl chloride and triphenylmethyl bromide in ether by decomposing the initial product with water. C. S.

Structure of Retene. Paul Lux (*Ber.*, 1910, **43**, 688—692. Compare Abstr., 1908, i, 873).—Retene is either 2-methyl-8-*iso*propyl- or 8-methyl-2-*iso*propyl-phenanthrene [compare following abstract]. The mono-oxime of retenequinone undergoes the Beckmann rearrangement when heated with acetic acid, acetic anhydride, and hydrogen chloride, forming one of the two possible *nitriles* of *methyl*-iso*propyldiphenic acid*, $CN \cdot C_6H_3R \cdot C_6H_3R' \cdot CO_2H$, where R and R′ are the alkyl residues. This acid has m. p. 112—114°, and forms on hydrolysis the corresponding *methyl* iso*propyldiphenamic acid*,

$$NH_2 \cdot CO \cdot C_6H_3R \cdot C_6H_3R' \cdot CO_2H,$$

m. p. 202—204°.

The nitrile interacts with thionyl chloride, forming the *chloride*, $CN \cdot C_6H_3R \cdot C_6H_3R' \cdot COCl$, m. p. 96—97°, decomp. 150°; it is converted into the *amidenitrile* on treatment with ammonia in benzene solution. This has m. p. 141—142·5°, and is hydrolysed to the *diamide*, $NH_2 \cdot CO \cdot C_6H_3R \cdot C_6H_3R' \cdot CO \cdot NH_2$, or by means of concentrated alcoholic potassium hydroxide to the second *methyl*iso*propyldiphenamic acid*, $CO_2H \cdot C_6H_3R \cdot C_6H_3R' \cdot CO \cdot NH_2$, m. p. 194—196°, decomp. 210°. When heated it probably forms the *diphenimide*, $\begin{matrix} R \cdot C_6H_3 \cdot CO \\ R' \cdot C_6H_3 \cdot CO \end{matrix} > NH$.

E. F. A.

Constitution of Retene and its Derivatives. John E. Bucher (*J. Amer. Chem. Soc.*, 1910, **32**, 374—382).—In the course of a study of the condensation of acids of the phenylpropiolic series to derivatives of 1-phenyl-2 : 3-naphthalenedicarboxylic acid (Abstr., 1908, i, 791), it was found that the constitution of most of these compounds could be ascertained by converting them into diphenyltetracarboxylic acid or by oxidising them to benzenepolycarboxylic acids. These methods have now been applied to the determination of the constitution of retene (methyl*iso*propylphenanthrene).

When a solution of retenequinone in pyridine is oxidised with potassium permanganate, it is converted into a mixture of acids, containing 3-*hydroxy*iso*propyldiphenyl*-1 : 1′ : 2′-*tricarboxylic acid*,

$$OH \cdot CMe_2 \cdot C_6H_3(CO_2H) \cdot C_6H_3(CO_2H)_2,$$

which loses water on heating, with formation of a residue soluble in sodium carbonate solution. The formation of this acid from retenequinone shows that two of the carboxyl groups occupy the 1- and 1′-positions, whilst the production of water on heating indicates the presence of another carboxyl group in the 2′-position. As the *iso*propyl residue still remains, the 2′-carboxyl group must have been derived from the methyl group, which therefore occupies the 8-position

in retene. When this tricarboxylic acid is further oxidised, it yields the corresponding tetracarboxylic acid, together with a small quantity of benzene-1 : 2 : 3-tricarboxylic acid. The last mentioned acid is also formed, together with the 1 : 2 : 4-isomeride, by the oxidation of diphenyleneketonedicarboxylic acid which Bamberger and Hooker (Abstr., 1885, 905, 1070) obtained by the oxidation of retene. The production of these two acids shows that retene has one group in the 8-position and the other in either the 2- or 3-position, and excludes the formula proposed by Bamberger and Hooker (*loc. cit.*).

When the mixture of acids obtained by the oxidation of retenequinone is heated with potassium hydroxide at 218° and the resulting acids are reduced with hydriodic acid, a mixture of hydrocarbons is obtained, which, when oxidised with potassium permanganate, yields diphenyl-3-carboxylic acid. The *iso*propyl group in retene must therefore occupy the 2-position, and hence retene is 8-methyl-2-*iso*propylphenanthrene [compare preceding abstract].

It is pointed out that now the constitution of retene has been established, it will be necessary to correct the structural formulæ of its various derivatives. The constitution assigned to abietic acid by Easterfield and Bagley (Trans., 1904, **85**, 1238) is discussed. E. G.

Quantitative Development of the Sandmeyer Reaction. Gustav Heller (*Zeitsch. angew. Chem.*, 1910, **23**, 389—392).—The author has worked out the conditions under which the introduction of chlorine by the Sandmeyer reaction in the case of aniline, and *p*- and *o*-toluidines can be effected almost quantitatively. The most important factor is the concentration of the hydrochloric acid in the solution ; if rather more acid is taken than is recommended by Erdmann (Abstr., 1893, i, 151), the separation of a solid intermediate product does not occur, and the rise in temperature necessary to decompose it may be avoided. The reaction is therefore carried out at a lower temperature than is possible under the conditions given by Erdmann. It is probable that the intermediate compounds formed in these circumstances are very soluble complex salts of cuprous chloride.

R. V. S.

Preparation of 1-Naphthylamine-4 : 7-disulphonic Acid and of -2 : 4 : 7-trisulphonic Acid from 1 : 8-Dinitronaphthalene. Farbwerke vorm Meister, Lucius & Brüning (D.R.-P. 215338).—When 1 : 8-dinitronaphthalene is reduced in aqueous solution with sodium sulphite, sodium ammonium sulphite, or ammonium sulphite at 70—90°, free alkali is produced ; this results from the entrance of sulphonic groups into the nucleus, and is accompanied by the elimination of a nitro-group.

If the solution is kept neutral, or only slightly alkaline, and the heating continued until the reaction is complete, there separates, when cool, colourless needles of *sodium* or *ammonium* 1-*naphthylsulphamin*-4 : 7-*disulphonate*, which on warming with mineral acid yields 1-naphthylamine-4 : 7-disulphonic acid, crystallising from hot water. The more soluble 1-*naphthylsulphamin*-2 : 4 : 7-*trisulphonates* remain in solution, from which, after heating with mineral acid, 1-naphthylamine-2 : 4 : 7-trisulphonic acid can be separated by means of salt. F. M. G. M.

α-*p*-Hydroxyphenylethylamine and the Synthesis of Hordenine, an Alkaloid in Malt Germs. Karl W. Rosenmund (*Ber.*, 1910, 43, 306—313).—β-*p*-Methoxyphenylethylamine hydrochloride (this vol., i, 106) is heated with alcoholic potassium hydroxide and methyl iodide at 100°, the product is treated with water and a little ether, the methiodide of the tertiary base is removed, and the mixture of primary, secondary, and tertiary bases, obtained by the evaporation of the filtrate, is heated with acetic anhydride; after the addition of water and ether, the tertiary base alone remains in the aqueous solution as the acetate. It is liberated by sodium hydroxide, extracted with ether, and demethylated by hydriodic acid. The product is β-*p*-hydroxyphenylethyldimethylamine (hordenine),

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2$$

(compare Léger, Abstr., 1906, i, 204), its identity with the natural alkaloid being proved, not only by its physical properties, but also by the identity of the methiodides; the latter is also produced by heating β-*p*-methoxyphenylethyltrimethylammonium iodide with hydriodic acid.

α-p-*Methoxyphenylethylamine*, $OMe\cdot C_6H_4\cdot CHMe\cdot NH_2$, b. p. 125—126°/16 mm., is a strongly basic oil obtained by reducing an alcoholic-acetic acid solution of the oxime of *p*-methoxyacetophenone by sodium amalgam; its *hydrochloride* has m. p. 160°. When heated with alcoholic potassium hydroxide and methyl iodide (3 mols.) it yields a *substance*, which melts at 162°, suddenly solidifies again, and then has m. p. 250°. When heated with hydriodic acid, however, α-p-*hydroxyphenylethylamine* is obtained in crystals, m. p. 120—121°. The *hydrochloride* forms needles, m. p. 185°. C. S.

p-Tolylethylamine and its Optically Active Forms. G. A. Stenberg (*Zeitsch. physikal. Chem.*, 1910, 70, 534—535).—α-p-*Tolylethylamine*, $C_6H_4Me\cdot CHMe\cdot NH_2$, has been prepared by transforming *p*-tolyl methyl ketone into the oxime, and then reducing with sodium amalgam in a solution slightly acidified with acetic acid. It is a colourless liquid, b. p. 204°; $D^{20} = 0{\cdot}937$.

By repeated fractional crystallisation of its salt with *l*-malic acid (the acid salt), the pure *d*-form of the base was obtained; $D^{20} = 0{\cdot}9366$; $[\alpha]_D^{20} = +36{\cdot}57°$. Similarly, the *l*-form has been obtained by fractional crystallisation of the acid salt which the base forms with camphoric acid; $D^{20} = 0{\cdot}7375$; $[\alpha]_D^{20} = +36{\cdot}23°$. The sulphates and oxalates of the active salts are considerably more soluble than the racemic salts.

Xylylethylamine is now being investigated; the *l*-form of the salt has already been prepared. G. S.

Isomeric Arylimines of Unsaturated Ketones. Fritz Straus and A. Ackermann (*Ber.*, 1910, 43, 596—608).—Ammonia does not react with the keto-dichloride of *p*-chlorophenyl *p*-chlorostyryl ketone (Abstr., 1909, i, 489), but *p*-nitroaniline reacts in the normal manner, yielding *p*-nitroanilino-*p*-chlorophenyl-*p*-chlorostyrylmethyl chloride, $C_6H_4Cl\cdot CH{:}CH\cdot CCl(C_6H_4Cl)\cdot NH\cdot C_6H_4\cdot NO_2$. The chlorine atom of the CCl group is not reactive; for example, the compound dissolves in concentrated sulphuric acid without evolution of hydrogen chloride. It reacts, however, with acids in hydroxylic solvents, yielding the

ketone. The chloride reacts with sodium methoxide or ethoxide, losing hydrogen chloride and yielding the *p*-nitrophenylimine,

$$C_6H_4Cl\cdot CH:CH\cdot C(C_6H_4Cl):N\cdot C_6H_4\cdot NO_2.$$

When *p*-toluidine is used instead of *p*-nitroaniline, an intermediate chloride is not obtained, but the tolylimine is formed immediately. The *p*-tolylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane exists in two isomeric modifications: a yellow and a colourless. They are both stable, and can be crystallised or fused without undergoing transformation; they yield isomeric salts, and can be recovered unaltered from these salts. The two compounds are regarded as stereoisomeric in the same sense as oximes and anils.

p-*Nitroanilino*-p-*chlorophenyl*-p-*chlorostyrylmethyl chloride*,

$$C_{21}H_{15}O_2N_2Cl_3,$$

crystallises in yellow plates, m. p. 118—119°. Its solution in concentrated sulphuric acid is yellowish-red and has a bluish-red dichroism.

The yellow p-*tolylimino*-p-*chlorophenyl*-p-*chlorostyrylmethane*,

$$C_6H_4Cl\cdot CH:CH\cdot C(C_6H_4Cl):N\cdot C_6H_4Me,$$

crystallises in soft, lustrous, yellow needles, m. p. 130—131°, and is the only product formed when the condensation is carried out at the ordinary temperature for some forty hours. The *picrate*,

$$C_{22}H_{17}NCl_2,C_6H_3O_7N_3,$$

crystallises in reddish-yellow needles, m. p. 167—168°, and when boiled with alcohol yields the ketone and *p*-toluidine picrate. The *hydrochloride*, $C_{22}H_{17}NCl_2,HCl$, has m. p. 170—171°. The *isomeric* *p*-tolylimine is formed when the reacting substances are left together for some weeks; it crystallises in colourless, glistening plates, m. p. 144—145°, and is not so readily soluble in most solvents or so readily burnt as is the yellow isomeride. The *picrate*,

$$C_{22}H_{17}NCl_2,OH\cdot C_6H_2(NO_2)_3,$$

forms heavy, yellow crystals, m. p. 102—103° (decomp.). These crystals contain benzene of crystallisation, and, after heating until constant in weight, have m. p. 116—117°. It is not decomposed when boiled with alcohol. The *hydrochloride* forms snow-white needles, m. p. 100—101°, and when heated at 110—115° decomposes, yielding *p*-chloroacetophenone and *p*-chlorophenyl *p*-chlorostyryl ketone.

J. J. S.

Coloured Additive Products of Aromatic Amines. The Question of the Mechanism of Substitution in the Benzene Nucleus. VII. Heinrich Wieland and Ernst Wecker (*Ber.*, 1910, 43, 699—712. Compare Abstr., 1907, i, 1076, and following abstract).—The authors have more fully investigated the strongly coloured, unstable compounds of tertiary and secondary amines with bromine and with the chlorides of the metalloids. They consider that these compounds are quinonoid additive products of the type $NAr_2Br:C_6H_4:MeBr$, which undergo spontaneous rearrangement, forming compounds with substituted benzene nuclei. The reaction in the case of the blue bromide of tri-*p*-tolylamine is expressed by the equation:

$$2N(C_6H_4Me)_3Br_3 = N(C_6H_3BrMe)_3 + N(C_6H_4Me)_3 + 3HBr.$$

Tri-*p*-tolylamine when treated with bromine in benzene solution at

$-15°$ yields a *tribromide*, $N(C_7H_7)_3Br_3$, which forms dark blue, crystalline scales. When a chloroform solution of the substance is kept at the ordinary temperature, *tribromotri*-p-*tolylamine*, m. p. 190°, and tri-*p*-tolylamine are formed. The dibromotri-*p*-tolylamine, m. p. 160—165°, formerly described (*loc. cit.*) is a mixture of tribromotri-*p*-tolylamine and tri-*p*-tolylamine. *Tri* p-*anisylamine*, prepared by Goldberg's method (Abstr., 1908, i, 17), has m. p. 94·5°. With bromine it yields a *tribromide*, $N(C_6H_4{\cdot}OMe)_3Br_3$, which crystallises in dark violet laminæ, and is very stable. In chloroform solution it slowly decomposes, forming *tribromotri*-p *anisylamine*, m. p. 179°, and tri-*p*-anisylamine. Tri-*p* anisylamine also forms a deep blue, crystalline *compound* with antimony pentachloride. *Diphenyl*-p-*anisidine*, $NPh_2{\cdot}C_6H_4{\cdot}OMe$, prepared by Goldberg's method, has m. p. 104°. The compounds of this substance with bromine and antimony pentachloride could not be isolated.

Diphenylamine and di-*p*-tolylamine do not give coloured additive products with bromine or antimony pentachloride; phenyl-*p*-anisidine gives colorations indicating the formation of such compounds, and from the solution, *tribromophenyl*-p-*anisidine*, m. p. 100·5°, is obtained. Phenyl-*p*-anisidine (compare Willstätter and Kubli, Abstr., 1909, i, 976) was prepared from aceto-*p*-anisidide by Goldberg's method. In the case of di-*p*-anisylamine, the colorations observed are abnormal, owing to the formation of some anisazonium bromide, which is red. The additive *bromide* can be obtained by working in ethereal solution as a dark bluish-green, flocculent precipitate, which can be filtered. On dissolving it in chloroform, rearrangement occurs so rapidly that the solution is colourless unless strongly cooled. In solvents other than ether, di-*p*-anisylamine and bromine directly yield *dibromodi*-p-*anisylamine*, m. p. 79°. When this is treated with a further quantity of bromine in benzene-chloroform solution, a green, crystalline, stable *dibromide*, $C_{14}H_{13}O_2NBr_2,Br_2$, is formed, m. p. 104° (decomp.). In chloroform solution it undergoes rearrangement, yielding, besides dibromodi-*p*-anisylamine, a mixture of *tribromodi*-p-*anisylamine*, m. p. 135·5°, and *tetrabromodi*-p-*anisylamine*, m. p. 183°. A *compound* of di-*p*-anisylamine and antimony pentachloride, $C_{14}H_{15}O_2N,SbCl_5$, is formed on mixing chloroform solutions of the two substances. It crystallises in dark steel-blue prisms, m. p. 116—118°, and is stable. From it, anisazonium chloride and di-*p*-anisyldihydroanisazine can be prepared (compare Abstr., 1908, i, 1015). R. V. S.

Oxidation of *p*-Anisidine and of Dimethyl-*p*-anisidine. Heinrich Wieland [with Ernst Wecker] (*Ber.*, 1910, 43, 712—728. Compare preceding abstract.)—The fact that the methoxylated amines yield coloured additive products with bromine, whilst the amines themselves do not, leads to the supposition that these additive products may be oximonium compounds of the type

$$OMe{\cdot}C_6H_4{\cdot}NHBr{:}C_6H_4{:}OBrMe.$$

The action of bromine on *p*-anisidine and on dimethyl-*p*-anisidine at low temperatures effects the removal of the methoxyl group with remarkable ease, the ultimate product of the oxidation being quinone.

The formation of *meri*-quinonoid and quinonoid bromine compounds as intermediate products also occurs, although these are less stable than the corresponding nitrogen derivatives (compare Willstätter and Piccard, Abstr., 1908, i, 475, 915).

p-Anisidine is oxidised by ferric chloride, chromic acid, hypochlorous acid, bromine, and other oxidising agents in acid solution with formation of a violet dye, which yields a leuco-base on reduction, indicating that several molecules of the amine have become united (compare Willstätter and Piccard, Abstr., 1909, i, 517). In acetic acid solution in the presence of sodium acetate, bromine water oxidises all the anisidine to the violet dye, which soon decomposes. When the oxidation is effected by bromine water at a low temperature, however, a pure blue coloration develops, which gradually becomes violet. It is probable that the blue colour is due to the *meri*-quinonoid additive product $\{OBrMe{:}C_6H_4{:}NH_2Br,OMe{\cdot}C_6H_4{\cdot}NH_2\}$. The violet dye only appears in acid solution when insufficient bromine is present; when the oxidation by bromine water in faintly acid solution is rapid and complete, the *p*-anisidine is converted almost quantitatively (98%) into quinone. In this reaction 2 molecules of free acid are formed, showing that hydrolysis of the methoxyl group occurs; this confirms the theory as to the primary formation of a quinonoid oximonium salt.

Aminophenol also yields quinone quantitatively when oxidised with bromine water under the above conditions (compare Willstätter and Dorogi, Abstr., 1909, i, 535), and in this case, also, the intermediate formation of quinonemonoimine (Willstätter and Pfannenstiel, Abstr., 1905, i, 69) is probable.

When treated with bromine in chloroform solution, *p*-anisidine yields a *dibromo*-p-*anisidine*, which crystallises in long needles, m. p. 81°. The bromination is accompanied by the development of an evanescent, blue colour, and when it is effected in ethereal solution, an unstable blue *compound* (perhaps the primary quinonoid product) can be isolated.

Dimethyl-*p*-anisidine (compare Griess, Abstr., 1880, 636) is obtained by methylating *p*-anisidine with methyl sulphate. It has m. p. 49° (Griess: 48°). The *chloride*, *bromide*, and *picrate* crystallise well. When the base is treated gradually with bromine in chloroform solution, a vivid red coloration is first produced, which gradually changes to a blue colour; eventually, the quinonoid *perbromide*, $OBrMe{:}C_6H_4{:}NMe_2Br_2$, is precipitated. It crystallises in small, lustrous, green laminæ, m. p. 49—50°, and on reduction yields dimethyl-*p*-anisidine. Its aqueous solution (which is orange) rapidly decomposes into quinone, dimethylamine hydrobromide, hydrobromic acid, and methyl alcohol. Oxidation of dimethyl-*p*-anisidine in aqueous solution with one molecule of bromine (in the form of bromine water) yields a quinonoid bromide of dimethylaminophenol, $NMe_2Br{:}C_6H_4{:}O$, in solution, for, on reducing the liquid, dimethylaminophenol is obtained. If a second molecule of bromine is added, however, the fairly stable, yellow *perbromide*, $NMe_2Br{:}C_6H_4{:}OBr_2$, m. p. 90°, is precipitated. On reduction, this yields almost quantitatively dimethyl-*p*-aminophenol, m. p. 78° (von Pechmann, Abstr., 1900, i, 173, gave

74—76°). When left in contact with water, the perbromide decomposes into quinone, dimethylamine hydrobromide, and bromine.

The estimation of quinone is effected by reducing to quinol, and titrating the latter with iodine in the presence of sodium hydrogen carbonate. On acidifying, the quinone liberates the iodine again, and, as a control, this may be titrated with thiosulphate. This is of value when traces of other oxidisable substances are present. The quinone in ethereal solutions may also be estimated by a modification of Nietzki's method.

Bromine is best recognised in the presence of quinonoid compounds and mineral acid by adding sodium acetate solution before testing with potassium iodide and starch paper, which is then only affected by the free halogen. R. V. S.

Carbodiphenylimide. Karl Schall (*J. pr. Chem.*, 1910, [ii], 81, 191—192).—The author disputes some of the statements concerning γ-carbodiphenylimide made in a footnote in Busch, Blume, and Punge's paper on carbodiphenylimide (Abstr., 1909, i, 565). C. S.

$\Delta^{1:5}$-Dihydrophenol. [Δ^{2}-*cyclo*-Hexenone.] Leo Tschugaeff (*J. pr. Chem.*, 1910, [ii], 81, 188—189).—Polemical. A reply to Kötz and Grethe (this vol., i, 24). The author claims priority for the method used to convert *cyclo*-hexanon-2-ol into $\Delta^{1:5}$-dihydrophenol, and dissents from these authors representing the xanthogenate as containing :C(OH)·CS·SMe in preference to the constitution, :CH·O·CS·SMe, usually accepted. C. S.

Phenol and *m*-Nitrophenol as Acids. Harald Lundén (*Zeitsch. physikal. Chem.*, 1910, 70, 249—255).—The acid dissociation constant, k_a, of phenol has been determined by measuring the electrical conductivity of solutions of the ammonium salt; the values are $k_a \times 10^{10} =$ 0·56 at 10°, 0·66 at 15°, 0·97 at 25°, 1·51 at 40°, and 2·05 at 50°. These values have been confirmed by direct determinations of the conductivity of aqueous solutions of phenol, and are also in good agreement with the results obtained by Buch (Abstr., 1908, i, 259).

The dissociation constant of *m*-nitrophenol has also been determined by conductivity measurements with carefully purified aqueous solutions; the values are $k_a \times 10^{9} = 3{\cdot}31$ at 10°, 3·91 at 15°, 5·33 at 25°, 7·72 at 40°, and 9·54 at 50°.

From the data for phenol, the heat of neutralisation with ammonia and the heat of dissociation have been calculated in the usual way; the value of the former is $7605 - 6{\cdot}5t$ cal., and of the latter, $-7095 + 43{\cdot}5t$ cal. per mol. Both values are in excellent agreement with the direct determinations of Berthelot (1873).

The heat of neutralisation of *m*-nitrophenol is $8520 - 2{\cdot}1t$ cal.; the heat of dissociation, $-6180 + 47{\cdot}9t$ cal.

The data for the influence of temperature on the total and free energy of the above changes are tabulated. G. S.

New Method of Formation of Ethers of Glycerol and Phenols. Petar Živković (*Monatsh.*, 1908, 29, 951—958).—A mixture

of a phenol or naphthol (1 part), glycerol (2 parts), and anhydrous sodium acetate (1 part), contained in a flask, in an atmosphere of coal gas, is heated for twelve to twenty hours by the vapour of ethyl benzoate. In the case of the phenols, the benzene extract of the product is directly precipitated with light petroleum; when dealing with α-naphthol, the mass is boiled with water and dried before being treated with benzene. In addition to glycerol phenyl ether, the following mono-ethers have been obtained: the *o-tolyl ether*, $C_7H_7\cdot O\cdot C_3H_5(OH)_2$, m. p. 66°; the *m-tolyl ether*, m. p. 65°; the *p-tolyl ether*, m. p. 73—74°; the *α-naphthyl ether*, m. p. 91—92°; *β-naphthyl ether*, m. p. 109—110°. None of the ethers give a colour reaction with ferric chloride, but form brown or green solutions in concentrated sulphuric acid when treated with potassium nitrite, which become green or red by dilution and the addition of alkali. C. S.

Amino-alcohols. Derivatives of Glycerol and Phenyl Ethers. Ernest Fourneau (*J. Pharm. Chim.*, 1910, [vii], 1, 55—61, 97—103).—The complex ethers obtained by the condensation of epichlorohydrin with phenols have been studied, and especially their reaction with amines.

When phenol or sodium phenoxide is heated in a closed tube with epichlorohydrin, the three chief products formed are: (1) phenyl glycide ether, $OPh\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ O\end{matrix}>$, b. p. 242·5°/755 mm. (compare Rössing, Abstr., 1886, 345; Lindemann, Abstr., 1891, i, 1198; Cohn and Plohn, Abstr., 1907, i, 605); (2) γ-chloro-β-hydroxy-α-phenoxypropane, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$, b. p. 170°/21 mm. (compare Lindemann, *loc. cit.*; Fischer and Krämer, Abstr., 1908, i, 858), and (3) glycerol diphenyl ether (Lindemann, *loc. cit.*). In some cases a small amount of *diphenoxydipropanol oxide*, $[OPh\cdot CH_2\cdot CH(OH)\cdot CH_2]_2O$, m. p. 81°, b. p. 300—305°/16 mm., is formed; it crystallises in colourless spangles.

Phenyl glycide ether reacts with water to form glycerol phenyl ether, m. p. 69°, and with alcohol to form *glycerol phenyl ethyl ether*, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OEt$, b. p. 158—160°/25 mm., a colourless, inodorous liquid. With magnesium ethyl bromide, *phenoxypropylene bromohydrin*, b. p. 160—162°/18 mm., is formed (compare Abstr., 1907, i, 817), but with magnesium phenyl bromide, *β-hydroxy-γ-phenoxy-α-phenylpropane*, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2Ph$, m. p. 91—92°, crystallising in spangles, is obtained.

In the action of epichlorohydrin on (*a*) *p*-cresol and (*b*) α-naphthol, the corresponding glycide ethers described by Lindemann (*loc. cit.*) are produced, and, in addition, *glycerol di-p-tolyl ether* in the one case and *glycerol di-α-naphthyl ether* (m. p. 116°) in the other.

The product obtained by the action of catechol on epichlorohydrin is not diglycidylcatechol as Lindemann supposed (*loc. cit.*), but is identical with Mourcu's substance obtained by condensing sodium catechol with αβ-dibromohydrin.

The *glycide ether*, prepared in an analogous manner from guaiacol, has b. p. 170°/16 mm. and m. p. 79·5°, whilst that from thymol boils at 180°/20 mm., melts at 88°, and crystallises in colourless needles.

By the action of sodium *p*-nitrophenoxide on dichlorohydrin, *glycerol di-*p-*nitrophenyl ether*, $OH\cdot CH(CH_2\cdot O\cdot C_6H_4\cdot NO_2)_2$, m. p. 122—123°, crystallising in bright yellow needles, is obtained, together with p-*nitrophenyl glycide ether*, m. p. 69°, which forms yellow tablets.

Phenyl glycide ether reacts with ammonia to form *diphenoxypropanolamine*, $NH[CH_2\cdot CH(OH)\cdot CH_2\cdot OPh]_2$, m. p. 97—98°; its *hydrochloride* has m. p. 175°.

The following amino-alcohols have been obtained in like manner by the action of appropriate amines on the glycide ethers described above.

γ-Dimethylamino-α-phenoxypropanol, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2$, has b. p. 161°/13 mm. or 169°/25 mm.; the *picrate*, m. p. 105°, crystallises in spangles; the *hydrochloride* of the *benzoyl* derivative, m. p. 166°, the *ethyl bromide* derivative, m. p. 112°, and other similar compounds were prepared. The corresponding *γ-anilino*-derivative,

$$OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NHPh,$$

has m. p. 57°, and the analogous *γ-phenetidino*-compound, m. p. 95°, both crystallise in colourless needles.

*γ-Dimethylamino-α-*p-*tolyloxypropanol*, b. p. 175—176°/10 mm., yields a *benzoyl* derivative, the *hydrochloride* of which has m. p. 156° and crystallises in slender needles.

γ-Dimethylamino-α-guaiacylpropanol, m. p. 61°, yields a *methiodide*, m. p. 114°, and a *benzoyl* derivative, the *hydrochloride* of which has m. p. 142°.

γ-Dimethylaminonaphthoxypropanol, m. p. 81—82°, b. p. 217°/11 mm., crystallises in slender needles, and yields a *methiodide*, m. p. 204°.

*γ-Dimethylamino-α-*p-*nitrophenoxypropanol* exists in two forms (tablets and prisms), both having m. p. 81—82°; the *picrate*, m. p. 153°, and the *hydrochloride* of the *benzoyl* derivative, m. p. 181°, were prepared.

γ-Dimethylamino-α-thymoxypropanol, b. p. 177°/11 mm., crystallises on cooling, and gives a *methiodide*, m. p. 160°.

The methods of preparing these substances are described in some detail in the original. As a rule, these amino-alcohols exhibit antipyretic and analgesic properties, but, owing to their cardiac action, they are unsuitable for therapeutic use in this way. T. A. H.

Preparation of Tribromocatechol. Chemische Fabrik von Friedr. Heyden (D.R.-P. 215337).—When catechol is treated with 3 mols. of bromine in acetic acid solution, no tribromocatechol is formed, the product consisting of a mixture of the di- and tetrabromo-derivatives.

Tribromocatechol, m. p. 138—139°, is obtained by the action of bromine in chloroform on a suspension of catechol in the same solvent; it is colourless, odourless, and insoluble in water, but readily soluble in alcohol, ether, or acetone, and contains 1 mol. of water of crystallisation. It is employed therapeutically, and also in the preparation of dyes. F. M. G. M.

Action of Phosphorus Trichloride on Guaiacol. Pierre Dupuis (*Compt. rend.*, 1910, 150, 622—623).—Three compounds may be formed when guaiacol is heated with phosphorus trichloride

according to the proportions in which these substances react. *Guaiacylphosphorus chloride*, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}PCl_2$, prepared at 115—120°, is a colourless, refractive liquid, b. p. 135°/13 mm., n_D^{21} 1·568. When dissolved in dry ether and treated with chlorine, a yellow *tetrachloride*, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}PCl_4$, is formed, which is converted by sulphur dioxide into Auger's compound, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}POCl_2$ (Abstr., 1908, i, 529).

Diguaiacylphosphorus chloride, $P(O{\cdot}C_6H_4{\cdot}OMe)_2Cl$, has b. p. 235°/13 mm., n_D^{21} 1·586 and forms a *trichloride*, $P(O{\cdot}C_6H_4{\cdot}OMe)_2Cl_3$, from which diguaiacyl phosphoryl chloride may be obtained by the action of sulphur dioxide. Triguaiacyl phosphite, $P(O{\cdot}C_6H_4{\cdot}OMe)_3$, b. p. 275—280°/13 mm., solidifies on cooling, forming octahedra, m. p. 59°. This is not identical with Ballard's compound obtained by the action of phosphorus trichloride on the sodium derivative of guaiacol (D.R.-P. 95578).

The foregoing compounds are soluble in ether and benzene, and undergo decomposition when treated with water. W. O. W.

Some Derivatives of Phloroglucinol and a New Synthesis of Benzoresorcinol [2 : 4-Dihydroxybenzophenone]. Emil Fischer (*Annalen*, 1910, 371, 303—318).—2 : 4-Dihydroxybenzophenone may be prepared by hydrolysing the product formed by the interaction of benzene, aluminium chloride, and 2 : 4-dimethylcarbonatobenzoyl chloride (compare Abstr., 1909, i, 161).

Phloroglucinolcarboxylic acid reacts with only 1 mol. of methyl chlorocarbonate in *N*-sodium hydroxide solution; all attempts to obtain the corresponding trimethylcarbonato-derivative were unsuccessful; consequently 2 : 4 : 6-trihydroxybenzophenone could not be prepared in the same way as 3 : 4 : 5-trihydroxybenzophenone (compare Abstr., 1909, i, 309). Attempts to prepare 2 : 4 : 6-trihydroxybenzophenone by other methods were unsuccessful, but many new benzoyl derivatives of phloroglucinol have been obtained, the most interesting of which are the dibenzoyl derivatives of phloroglucinol dialkyl ethers; these probably have the constitution represented by one of the the following formulæ: $\begin{matrix} CBz{:}C(OR){\cdot}CH \\ \| \quad\quad\quad | \\ C(OH){:}CBz{\cdot}C{\cdot}OR \end{matrix}$ or $\begin{matrix} CBz{:}C(OR){\cdot}CBz \\ \| \quad\quad\quad | \\ C(OH){:}CH{\cdot}C{\cdot}OR \end{matrix}$, and, similarly to hydrocotoin (*C*-benzoylphloroglucinol dimethyl ether), are stable towards warm aqueous alkali; in this respect they differ from triacetyl*cyclo*hexanetrione and its tribenzoyl derivative (compare Heller, Abstr., 1909, i, 656).

1 : 3 : 5-*Trimethylcarbonatobenzene*, $C_6H_3(O{\cdot}CO_2Me)_3$, prepared by acting on a solution of phloroglucinol in a *N*-solution of sodium hydroxide with methyl chlorocarbonate, crystallises in long, glistening prisms, m. p. 99—100° (corr.); 4-*methylcarbonato*-2 : 6-*dihydroxybenzoic acid*, $CO_2Me{\cdot}O{\cdot}C_6H_2(OH)_2{\cdot}CO_2H$, similarly prepared from phloroglucinolcarboxylic acid, crystallises in tufts of flexible needles, m. p. 162° (corr., decomp.).

Benzoylphloroglucinolcarboxylic acid, $OBz{\cdot}C\lessdot\begin{matrix}CH{\cdot}C(OH)\\CH{:}C(OH)\end{matrix}\gtrdot C{\cdot}CO_2H$, prepared from phloroglucinolcarboxylic acid and benzoyl chloride, crystallises in small prisms, m. p. 195° (corr., decomp.); the *silver* salt is a colourless, crystalline powder; the acid loses carbon dioxide when

heated at 200°, yielding *benzoylphloroglucinol*, $C_{13}H_{10}O_4$, which forms slender leaflets and needles, m. p. 198—199° (corr.).

O-*Benzoylphloroglucinol diethyl ether*, $C_6H_3(OEt)_2 \cdot OBz$, is formed by acting on phloroglucinol diethyl ether with benzoyl chloride and alkali; it crystallises in colourless, slender, pointed prisms and needles, m. p. 84° (corr.), and when heated with benzoyl chloride and zinc chloride in benzene yields *tribenzoylphloroglucinol diethyl ether*, $CHBz_2(OEt_2) \cdot OBz$, which crystallises in microscopic, long, slender plates, m. p. 163—164° (corr.); the latter substance is converted by an alcoholic solution of potassium hydroxide under pressure at 100° into C-*dibenzoylphloroglucinol diethyl ether*, $C_6HBz_2(OEt)_2 \cdot OH$, which forms slightly yellow, microscopic, rhomboidal leaflets, m. p. 156° (corr.); the *potassium* salt forms glistening, pale yellow leaflets; the *sodium* salt crystallises in slender needles.

Tribenzoylphloroglucinol dimethyl ether, $C_{29}H_{22}O_6$, may be prepared by treating either the monobenzoyl compound or hydrocotoin with benzoyl chloride and zinc chloride in benzene; it crystallises in microscopic plates, m. p. 198° (corr.); C-*dibenzoylphloroglucinol dimethyl ether*, $C_{22}H_{18}O_5$, crystallises in microscopic needles and plates, m. p. 170° (corr.); the *potassium* salt, $C_{22}H_{17}O_5K$, forms yellow, microscopic plates. W. H. G.

Derivatives of Triphenylcarbinol. II. Adolf von Baeyer [and, in part, Aickelin, Carl Diehl, Hallensleben, and Hermann Hess] (*Annalen*, 1910, **372**, 80—151. Compare Abstr., 1907, i, 757).—The present communication contains the results of a systematic investigation of the binary derivatives of triphenylcarbinol, namely, those containing two hydroxyl or amino-groups in at least one of the benzene nuclei.

I. *Binary Dihydroxy-derivatives.*—(1) *Dihydroxytriphenylcarbinols.*—2 : 5-*Dihydroxytriphenylcarbinol*, $C_{19}H_{16}O_3$, prepared by Grignard's reaction from ethyl 2 : 5-dihydroxybenzoate and bromobenzene, has m. p. 136°; it crystallises with $\frac{1}{2}C_6H_6$ in colourless, glistening leaflets, m. p. 110° (decomp.); a green *substance*, which probably has the formula $C_6H_3(OH)_2 \cdot CPh_2Cl,HCl$, is obtained by passing hydrogen chloride into an ethereal solution of the carbinol and evaporating in a vacuum desiccator over potassium hydroxide; it dissolves in ether, forming a colourless solution of the carbinyl *chloride*, $C_6H_3(OH)_2 \cdot CPh_2Cl$, which, when treated with alkalis, assumes a transient, blue colour, owing to the formation of an unstable *o*-fuchsone with a hydroxyl group in the quinonoid ring, $\begin{matrix} C(ONa):CH\cdot C:CPh_2 \\ | \qquad\qquad | \\ CH{=}{=}CH\cdot C:O \end{matrix}$.

The compounds described immediately were prepared in an unsuccessful attempt to obtain a *p*-fuchsone with a hydroxyl group in the quinonoid nucleus.

Methyl 2 : 4-*dihydroxybenzoate*, $C_8H_8O_4$, crystallises in colourless, glistening rhombohedra, m. p. 117—118°; when treated with magnesium phenyl bromide, it yields a red tar, from which 2 : 4-dihydroxytriphenylcarbinol could not be isolated.

2 : 4-*Dihydroxytriphenylcarbinol*, $C_{19}H_{16}O_3$, is prepared by Grignard's reaction from 2 : 4-dihydroxybenzophenone and bromobenzene; it

crystallises in colourless prisms, m. p. 124° (decomp.), and is hydrolysed by aqueous sodium hydroxide, yielding benzophenone, resorcinol, 2 : 4-dihydroxybenzophenone, and benzene; the *perchlorate*, $C_{19}H_{15}O_6Cl$, forms large, brown plates, and explodes slightly when heated; all attempts to isolate the corresponding fuchsone were unsuccessful; when a solution of the carbinol in nitrobenzene is heated at 100°, it yields a *substance*, which crystallises in dark brown needles, m. p. 264°.

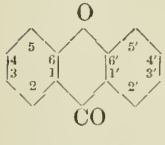
2 : 4-*Dihydroxy*-4′-*methoxytriphenylcarbinol*, $C_{20}H_{18}O_4$, prepared from 2 : 4-dihydroxy-4′-methoxybenzophenone and bromobenzene, crystallises in colourless prisms, m. p. 138—139° (decomp.).

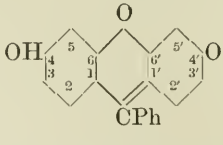
(2) *Dihydroxydiphenylphthalides.*—2 : 4-Dihydroxydiphenylphthalide is best prepared by the action of concentrated sulphuric acid on a cold fused mixture of *o*-benzoylbenzoic acid and resorcinol; contrary to von Pechmann (Abstr., 1882, 184), it has m. p. 198—199°, and does not give a coloration when the solution in glacial acetic acid is treated with concentrated hydrochloric acid; the solution in aqueous alkalis is orange, and probably contains the fuchsone derivative,

$$CO_2Na\cdot C_6H_4\cdot CPh{:}C\!<\!\begin{matrix}CH{=\!=}CH\\ C(OH){:}CH\end{matrix}\!>\!CO.$$

3 : 4-*Dihydroxydiphenylphthalide*, $C_{20}H_{14}O_4$, forms colourless prisms, m. p. 160—161°. 2 : 5-*Dihydroxydiphenylphthalide* crystallises in needles and prisms, m. p. 246—247° (decomp.), and dissolves in aqueous sodium hydroxide in the absence of oxygen, forming a blue solution which becomes colourless when kept, but in the presence of air turns brown, owing to oxidation; the blue solution undoubtedly contains the *salt*, $CO_2Na\cdot C_6H_4\cdot CPh{:}C\!<\!\begin{matrix}CO{-\!-}CH\\ CH{:}C(OH)\end{matrix}\!>\!CH$; the corresponding *quinone*, $C_{20}H_{12}O_4$, obtained by treating an ethereal solution of the dihydroxy-compound with silver oxide, forms aggregates of dark yellow crystals, m. p. 147°; the latter substance forms a *quinhydrone* with quinol; the dihydroxy-compound also forms a *quinhydrone* with *p*-benzoquinone, but not with its own quinone.

II. *Unitary-binary Trihydroxy-derivatives.* — *Trihydroxytriphenylcarbinols.* — Since xanthen is a saturated compound, the author proposes to designate this substance xanthan; the use of the annexed system of numbering the positions in





xanthone and resorcinolbenzein is advocated [but is not adopted in this abstract] as the author dissents from that used in Beilstein [and in this Journal].

o-3-*Methoxyphenoxybenzoic acid*, $OMe\cdot C_6H_4\cdot O\cdot C_6H_4\cdot CO_2H$, prepared by Ullmann's method (Abstr., 1905, i, 597) from *o*-chlorobenzoic acid and 3-methoxyphenol, crystallises in colourless, silky needles, m. p. 132°; when treated in benzene with phosphorus pentachloride and subsequently with aluminium chloride, it yields 3-*methoxyxanthone*,

$$C_6H_4\!<\!\begin{matrix}O{-\!-}C{:}CH\cdot C\cdot OMe\\ CO\cdot C{:}CH\cdot CH\end{matrix}\!>$$

which forms tufts of colourless needles or leaflets, m. p. 132°. The latter substance is converted by magnesium phenyl bromide into

3-methoxy-9-phenylxanthen-9-ol, $C_6H_4<\begin{matrix}O\\CPh(OH)\end{matrix}>C_6H_3\cdot OMe$, which crystallises in colourless prisms, m. p. 127°, and, when treated with a solution of aluminium chloride in antimony trichloride, yields phenylfluorone, m. p. 207° (compare Kehrmann and Dengler, Abstr., 1908, i, 1002).

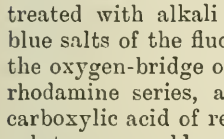
2-Methoxyxanthone has m. p. 135° (compare Ullmann, *loc. cit.*); *2-methoxy-9-phenylxanthen-9-ol*, $C_{20}H_{16}O_3$, crystallises in short prisms and plates, m. p. 136°; 2-hydroxy-9-phenylxanthen-9-ol has m. p. 170° (compare Kropp and Decker, Abstr., 1909, i, 248).

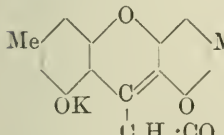
4-Methoxy-9-phenylxanthen-9-ol crystallises in colourless prisms, m. p. 172°; *4-hydroxy-9-phenylxanthen-9-ol*, $C_{19}H_{14}O_3$, forms bundles of small needles, m. p. 162°.

III. *Binary Tetrahydroxy-derivatives.*—(1) *Resorcinol group in the* o:p-*position.*—Fluorescein hydrochloride (compare Gattermann, Abstr., 1899, i, 513) is readily obtained in hexagonal leaflets by treating fluorescein with concentrated hydrochloric acid.

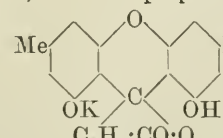
The nature of the changes which take place when fluorescein is treated with alkali is discussed. The conclusion is drawn that the blue salts of the fluorescein group result from the hydrolytic fission of the oxygen-bridge of the xanthone nucleus, and contain, at least in the rhodamine series, an ortho-quinonoid group. Since fluorescein is a carboxylic acid of resorcinolbenzein, it seemed probable that the latter substance would yield a violet salt when warmed with aqueous potassium hydroxide; under certain conditions an evanescent, violet coloration is obtained, which seems to point to the formation of an unstable violet salt with fission of the oxygen-bridge.

(2) *Resorcinal group in the* o : o′-*position.*—Meyer's α-orcinolphthalein (Abstr., 1897, i, 70) undoubtedly has the annexed constitution, since it corresponds completely with *vic.*-resorcinolbenzein (1 : 8-dihydroxy-9-phenylxanthen-9-ol) in properties; it is proposed, therefore, to designate this compound *vic.*-orcinolphthalein. The addition of alcoholic potassium hydroxide to an alcoholic solution of *vic.*-orcinolphthalein produces a violet coloration, probably owing to the formation of a *salt* having the constitution (I); the colour, however, disappears rapidly, and a colourless *potassium* salt (II) separates in elongated, rectangular prisms; the latter substance, when warmed with concentrated aqueous potassium hydroxide, yields a blue *potassium* salt, crystallising in prisms, which probably has the formula (III); an analogous *sodium* salt, crystallising in slender, violet needles, has been prepared.





(I.)



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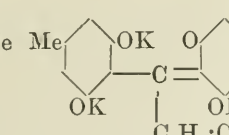
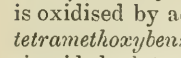
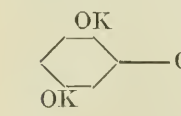


(III.)

2 : 6 : 2′ : 6′-*Tetramethoxydiphenylcarbinol*, $CH[C_6H_3(OMe)_2]_2\cdot OH$, is

prepared by Grignard's reaction from 2-iodoresorcinol dimethyl ether and ethyl formate (compare Kauffmann and Franck, Abstr., 1907, i, 1094); it crystallises in colourless, hexagonal prisms, m. p. 179°, and is oxidised by acetic acid and sodium dichromate, yielding 2 : 6 : 2′ : 6′-*tetramethoxybenzophenone*, $C_{17}H_{18}O_5$, which forms colourless, elongated, six-sided plates, m. p. 204°. The latter substance when treated with a solution of aluminium bromide in benzene yields 1 : 8-*dihydroxyxanthone*,  , which crystallises in tufts of pale yellow leaflets, m. p. 187°, and interacts with magnesium phenyl bromide, yielding 1 : 8-*dihydroxy*-9-*phenylxanthen*-9-*ol*, $C_{19}H_{14}O_4$, which forms elongated, hexagonal, and rhombic plates; the carbinyl *chloride* crystallises in black, opaque needles.

3. *Quinol group.*—Quinolphthalein, unlike *vic.*-orcinolphthalein, does not yield a violet salt when treated with a small quantity of alcoholic potassium hydroxide, probably because the formation of an ortho-quinonoid grouping without fission of the oxygen-bridge is impossible; a violet solution is obtained, however, when a large excess of alkali is employed; it probably contains the *salt* (annexed constitution), and when acidified yields the parent substance.



Quinolbenzein (2 : 7-dihydroxy-9-phenylxanthen-9-ol) may be prepared by hydrolysing 2 : 5 : 2′ : 5′-tetramethoxytriphenylcarbinol with a solution of aluminium chloride in antimony trichloride, or, more readily, by the phenylation and subsequent hydrolysis of 2 : 7-dimethoxyxanthone. The latter substance may be prepared from 5-methoxy-2-*p*-anisyloxybenzoic acid by treatment with hot concentrated sulphuric acid, but is more readily obtained from the dihydroxyxanthone prepared by Graebe from *β*-dinitroxanthone (compare Abstr., 1890, 504), thereby showing that the hydroxyl groups in this compound occupy the 2 : 7-positions.

2 : 5 : 2′ : 5′-Tetramethoxytriphenylcarbinol may be prepared by the action of benzotrichloride and aluminium chloride on quinol dimethyl ether; it crystallises in colourless plates and prisms, m. p. 125° (compare Kauffmann and Fritz, Abstr., 1909, i, 99).

5-*Methoxy*-p-*anisylsalicylic acid* (5-*methoxy*-2-p-*methoxyphenoxybenzoic acid*), $C_{15}H_{14}O_5$, prepared by the interaction of 2-chloro-5-methoxybenzoic acid and 4-methoxyphenol in the presence of copper powder, crystallises with $\frac{1}{2}H_2O$; the anhydrous substance has m. p. 95°.

2 : 7-Dihydroxyxanthone is best prepared from 2 : 7-diaminoxanthone by warming the diazonium sulphate with 70% sulphuric acid; when treated with methyl sulphate it yields 2 : 7-*dimethoxyxanthone*, $C_{15}H_{12}O_4$, yellow needles, m. p. 180°, which interacts with magnesium phenyl bromide, yielding 2 : 7-*dimethoxy*-9-*phenylxanthen*-9-*ol*, $C_{21}H_{18}O_4$, colourless prisms, m. p. 153°. The latter substance, when hydrolysed by aluminium bromide in benzene, yields *quinolbenzein*, the *chloroform* compound of which, $2C_{19}H_{14}O_4,CHCl_3$, forms small, colourless prisms

and decomposes at 100°; the *chloride*, $C_{19}H_{13}O_3Cl$, crystallises in brilliant red prisms or leaflets, and is not readily hydrolysed by water. The black *substance* obtained by heating the chloroform compound at 100° is probably an anhydride of the ortho-quinonoid form of the carbinol, or a mixed anhydride of the carbinol with the ortho-quinonoid form.

4. *Euxanthone group.*—*Phenyleuxanthenol dimethyl ether* (2 : 8-*dimethoxy*-9-*phenylxanthen*-9-*ol*), $C_{21}H_{18}O_4$, results from the interaction of magnesium phenyl bromide and euxanthone dimethyl ether; it crystallises in colourless prisms, m. p. 164—165°, and when treated with aluminium chloride in antimony trichloride yields 9-*chloro*-2 : 8-*dihydroxy*-9-*phenylxanthen*, $C_{19}H_{13}O_3Cl$, a violet-black, crystalline powder; the corresponding *carbinol* is obtained as a greyish-white, flocculent precipitate by adding acetic acid to a solution of the chloride in an excess of aqueous sodium hydroxide; it could not be obtained in a crystalline form; the carbinol chloride is converted (1) by aqueous ammonia into the corresponding *amide*, $C_{19}H_{15}O_3N$, which crystallises with $1C_5H_5N$ in colourless prisms and turns bluish-black when heated; (2) by an alcoholic solution of sodium ethoxide into the carbinyl *ethyl ether*, $C_{21}H_{18}O_4$, which forms colourless prisms and rhombic plates, m. p. 118—120° (decomp.), and when heated at about 130—140° yields the *anhydride* of the carbinol, $C_{19}H_{12}O_3$, a bluish-black powder.

W. H. G.

Derivatives of Amino-acids. III. Compounds with Cholesterol. Emil Abderhalden and Karl Kautzsch (*Zeitsch. physiol. Chem.*, 1910, 65, 69—77. Compare this vol., i, 226).—Chloroacyl chlorides react with cholesterol, yielding chloroacyl derivatives of the alcohol, but it has not been found possible to replace the halogen in these compounds by the amino-group, as ammonia simply hydrolyses the acyl derivatives to cholesterol and the acid amide.

Cholesteryl α-bromoisovalerate, $CHMe_2\cdot CHBr\cdot CO\cdot O\cdot C_{27}H_{34}$, crystallises in rhombic plates, sinters at 130°, and has m. p. 134·2—135·2° (corr.).

Cholesteryl α-bromoisohexoate crystallises in needles.

Glycylcholesterol hydrochloride, $C_{27}H_{43}\cdot O\cdot CO\cdot CH_2\cdot NH_2,HCl$, obtained by the action of glycyl chloride hydrochloride on cholesterol in the presence of chloroform, crystallises in slender needles, which decompose at 250°. The free *base*, $C_{27}H_{43}\cdot O\cdot CO\cdot CH_2\cdot NH_2$, has m. p. 140·5° (corr.), and $[\alpha]_D^{20}$ −24·98° in chloroform solution.

Cholesteryl isobutyrate, $CHMe_2\cdot CO\cdot O\cdot C_{27}H_{43}$, crystallises in plates, has m. p. 125° (corr.), after sintering at 108°, and has $[\alpha]_D^{20}$ −31·05° in chloroform solution.

Cholesteryl isovalerate, $CHMe_2\cdot CH_2\cdot CO\cdot O\cdot C_{27}H_{43}$, has m. p. 114°, and $[\alpha]_D^{20}$ −32·7°. *Cholesteryl laurate*, $C_{11}H_{23}\cdot CO\cdot O\cdot C_{27}H_{43}$, crystallises in slender needles, has m. p. 110°, after sintering at 78°, and $[\alpha]_D^{20}$ −31·3°. *Cholesteryl palmitate*, $C_{15}H_{31}\cdot CO\cdot O\cdot C_{27}H_{43}$, has m. p. 78·5—79·5° (corr.) and $[\alpha]_D^{20}$ −24·2°, and the *stearate*,

$$C_{17}H_{35}\cdot CO\cdot O\cdot C_{27}H_{43},$$

has m. p. 85—90°.

Resorcinol dichloroacetate, $C_6H_4(O\cdot CO\cdot CH_2Cl)_2$, crystallises in four-sided, colourless prisms, m. p. 71·5—72°. *Catechol dichloroacetate* crystallises in brilliant, long, colourless prisms, m. p. 57·5—58°, and *quinol dichloroacetate* in brilliant plates, m. p. 127°. The compounds are hydrolysed by ammonia to the phenol and chloroacetamide. J. J. S.

The Cholesterol Group. VI. Bombicesterol and the Presence of Cholesterol in the Chrysalis of the Silkworm. Angelo Menozzi and A. Moreschi (*Atti R. Accad. Lincei*, 1910, i, 126—129. Compare Abstr., 1908, i, 265).—The authors find that the chrysalis of the silkworm contains two members of the cholesterol group, namely, bombicesterol and ordinary cholesterol, the latter constituting about 13—14% of the mixture. Various hydrocarbons are also present. The following new derivatives of bombicesterol have been prepared.

Dihydrobombicesterol, obtained by passing hydrogen through an ethereal solution of bombicesterol in presence of platinum-black, has m. p. 134°, $[\alpha]_D^{19}$ +19·11°; it gives an *acetyl* derivative, m. p. 128°, $[\alpha]_D^{17}$ +13·45°. T. H. P.

Action of Nascent Hypoiodous Acid on Unsaturated Acids. *α-cyclo*Geranic Acid. J. Bougault (*Compt. rend.*, 1910, **150**, 397—399. Compare Abstr., 1905, i, 9; 1906, i, 848; 1908, i, 179, 269, 537, 983).—When *α-cyclo*geranic acid is dissolved in moist ether and treated with iodine and mercuric oxide, it undergoes oxidation with loss of carbon dioxide. In addition to substances of high boiling point, the product contains Wallach's trimethyl*cyclo*hexenone, $C_9H_{14}O$ (Abstr., 1902, i, 805), together with the corresponding alcohol, 1 : 3 : 3-*trimethyl*-Δ^1-cyclo*hexene*-6-*ol*, $C_8H_{16}O$. The latter was isolated by means of its phthalyl derivative, and obtained as a viscous liquid with a camphoraceous odour, b. p. 193°/760 mm., D_4^{17} 0·9310. The *acetate* has b. p. 206—207°. On oxidation it yields *αα*-dimethylglutaric acid, the ketone being formed as an intermediate product.

W. O. W.

***α-cyclo*Geranic Acid.** J. Bougault (*Compt. rend.*, 1910, **150**, 534—535. Compare preceding abstract).—Mercuric *α-cyclo*geranate decomposes in aqueous solution, liberating carbon dioxide and forming a complex liquid mixture, identical with that obtained by the action of nascent hypoiodous acid on *α-cyclo*geranic acid. When the latter substance is added to a boiling solution of mercuric acetate in acetic acid, a good yield of trimethyl*cyclo*hexenyl acetate is obtained; this is readily hydrolysed, thus affording a convenient method for the preparation of trimethyl*cyclo*hexenol.

Trimethyl*cyclo*hexenone is readily prepared by heating the alcohol on the water-bath, when it rapidly undergoes oxidation. W. O. W.

[Dichlorobenzoic Acids and Substances Derived Therefrom.] Fritz Ullmann and Carl Wagner (*Annalen*, 1910, **371**, 388. Compare Gomberg and Cone, this vol., i, 58).—The dichlorobenzoic acid employed in a recent investigation (compare Abstr., 1907, i, 846) was the 2 : 5- and not the 2 : 4-compound. The compounds obtained from

this acid are consequently 4-chlorodiphenylamine-2-carboxylic acid, 3-chloroacridone, 5-chloro-2-phenoxybenzoic acid, and 2-chloroxanthone. W. H. G.

Melting-point and Saturation Curves of Binary Systems; Substituted Benzoic Acids and Water. Otto Flaschner and Irvine Giles Rankin (*Monatsh.*, 1910, **31**, 23—50. Compare Trans., 1909, **95**, 668).—The solubilities of the hydroxy-, nitro-, amino-, and chloro-benzoic acids, of the toluic acids, and of *p*-bromobenzoic acid, *p*-iodobenzoic acid, *o*-phthalic acid, *p*-methoxybenzoic acid, *o*-acetoxybenzoic acid, and of 1 : 3 : 5-dinitrobenzoic acid in water have been determined by Alexéeff's method (Abstr., 1886, 847) in order to trace the relation between constitution and solubility, and the influence of the critical-solution point on the shape of the m.-p. curve. The results show that the introduction of a hydroxy-, amino-, nitro-, acetyl or carboxyl group into benzoic acid lowers the critical solution temperature, whilst the presence of a methyl or methoxyl group or of a halogen atom causes a rise. The influence of position is not always the same; the hydroxy- and the amino-groups have the greatest lowering effect in the para-, the nitro-group in the ortho-, position. The elevating influence of the methyl group is the same in all three positions, but that of the chlorine atom is greatest in the para-position. A comparison of the critical-solution point with any other property, such as the m. p. or the dissociation constant, shows that a close parallelism does not exist; the nearest agreement is shown in the case of the m. p.'s, the critical solution points and the m. p.'s of substituted benzoic acids containing the same group always changing in the order ortho, meta, para. C. S.

Action of Concentrated Sulphuric Acid on Some Aromatic Nitroamines. Frédéric Reverdin (*J. pr. Chem.*, 1910, [ii], **81**, 177—183; *Bull. Soc. chim.*, 1910, [iv], **7**, 130—136; *Compt. rend.*, 1910, **150**, 399).—The author gives instances of the reduction of the nitro- to the nitroso-group by concentrated sulphuric acid. Methyl 3 : 5-dinitro-4-nitromethylaminobenzoate, digested with sulphuric acid for twenty-four hours at the ordinary temperature, is converted into methyl 3 : 5-dinitro-4-nitrosomethylaminobenzoate and 3 : 5-dinitro 4-methylaminobenzoate; if the reaction is prolonged for six weeks, the first-mentioned ester and 3 : 5-dinitro-4-methylaminobenzoic acid are formed, the same result being obtained in two and a-half hours, however, at 40—60°. 2 : 4 : 6-Trinitronitromethylaniline yields trinitromethylaniline by heating with concentrated sulphuric acid for many hours on the water-bath. Grimaux and Lefèvre (Abstr., 1891, 1031), by the nitration of dimethyl-*o*-anisidine, obtained, amongst other products, the nitrosoamine and the nitroamine of 3 : 5-dinitromethylanisidine. The nitrosoamine is converted quantitatively into the nitroamine by fuming nitric acid in the cold. The nitroamine is remarkable in that it responds to Liebermann's test; it is converted into the nitrosoamine by concentrated sulphuric acid. C. S.

Partial Ester Formation of Benzoylaspartic Acid. Hermann Pauly and John Weir (*Ber.*, 1910, **43**, 661—670).—Half-esters of

benzoylaspartic acid may be produced either by opening the ring of the anhydride by means of methyl alcohol or by the partial hydrolysis of the normal ester with 1 mol. of alkali. The two methods yield the two isomeric half-esters practically free from admixture with their isomerides. That obtained from the anhydride is the *α-methyl ester-β-acid*, $CO_2Me\cdot CH(NHBz)\cdot CH_2\cdot CO_2H$; it is converted by phosphorus pentachloride into the *β-acid chloride*, and this by ammonia into the *β-amide*, which is identical with the compound obtained from benzoyl-*l*-asparagine by the action of methyl iodide on the silver salt. The half-ester from the normal ester is accordingly the *β-methyl ester-α-acid*, $CO_2H\cdot CH(NHBz)\cdot CH_2\cdot CO_2Me$.

Benzoylaspartic acid is about eight times as strong as succinic acid, whilst the α-ester-β-acid is six times, and the β-ester-α-acid sixteen times, as strong as the half-ester of succinic acid. It is the more strongly acid carboxyl which attracts the methyl group in the splitting of the anhydride and the metal when the normal ester is hydrolysed.

Benzoyl-*l*-aspartic acid has $K = 0{\cdot}0531$. The anhydride crystallises in asbestos-like needles, m. p. 208—209° (corr.). *α-Methyl β-hydrogen benzoylaspartate* forms minute needles, which sinter at 117—120°, m. p. 123—124°, $K = 0{\cdot}0186$. The *chloride*, prepared by the action of phosphorus pentachloride on the suspension of the acid in acetyl chloride in the absence of moisture by Fischer's method (Abstr., 1905, i, 863), forms minute needles, m. p. 143—144°. The *amide* forms needles, which sinter at 180°, m. p. 184°, $[\alpha]_D^{20}$, −14·03°; prepared by the esterification of benzoylasparagine, it had m. p. 184°, $[\alpha]_D^{20}$ −13·68°.

Benzoylasparagine, prepared by benzoylating *l*-asparagine, was obtained as needles, m. p. 190—196°, which contained about 10% of benzoylaspartic acid.

Dimethyl benzoylaspartate, prepared either by the action of methyl iodide on silver benzoylaspartate or by the action of methyl alcohol and dry hydrogen chloride on the acid, forms needles, m. p. 92·5° (corr.).

β-Methyl α-hydrogen benzoylaspartate forms prismatic plates, m. p. 154° (corr.), $K = 0{\cdot}0500$. It is less soluble than the isomeric acid.

E. F. A.

Preparation of Organic Dithionic Acids (Carbithionic Acids). Ignaz Bloch and Fritz Höhn (D.R.-P. 214888. Compare Abstr., 1906, i, 847; 1907, i, 382, 474).—The dithio-acids of general formula $R\cdot CS_2H$ have usually been prepared by the action of organo-magnesium compounds on carbon disulphide: which method is expensive and not of ready technical application.

It is found that dithio-acids are easily prepared by treating the corresponding aldehyde with hydrogen persulphide in the presence of condensing agents, such as zinc chloride, hydrogen chloride, or sulphuric acid, the reaction being general for both aliphatic and aromatic aldehydes.

Phenylcarbithionic acid (dithiobenzoic acid), $C_6H_5\cdot CS_2H$, is prepared from benzaldehyde, crude hydrogen persulphide, and zinc chloride, the excess of benzaldehyde being removed by steam; the *bismuth* salt is yellow; the *iron* salt, green and soluble in ether; the *methyl* ester, an

oil, b. p. 154—157°/22 mm.; the *ethyl* ester, a red oil, b. p. 165—168°/19 mm.

Thiobenzoyl disulphide, $S_2(CSPh)_2$, forms dark lilac needles, m. p. 117°: Houben (Abstr., 1906, i, 847) gives 92·5°.

Dithiosalicylic acid (*o-hydroxyphenylcarbithionic acid*), $HO{\cdot}C_6H_4{\cdot}CS{\cdot}SH$, m. p. 46—50°, is more stable, and separates from petroleum in orange-red needles; the *lead* salt crystallises from xylene in orange-red needles; the *methyl* ester is an orange oil of unpleasant odour; the *disulphide*, $S_2(CS{\cdot}C_6H_4{\cdot}OH)_2$, m. p. 122·5°, forms brown leaflets with a blue, metallic lustre.

Dithioanisic acid (p-*methoxyphenylcarbithionic acid*), $CH_3O{\cdot}C_6H_4{\cdot}CS_2H$, forms dark rose-coloured, oxidisable crystals; the *lead* salt separates from xylene in orange-yellow needles; the *zinc* salt forms rhombic, yellow crystals; the *mercury* salt, glistening, brown needles; the *bismuth* salt is yellow; the *methyl* ester, m. p. 31°, forms lake-red leaflets; the *ethyl* ester, red crystals; the *disulphide*, $S_2(CS{\cdot}C_6H_4OMe)_2$, dark red crystals, and has m. p. 163°. These compounds are therapeutically active, and are intermediate products in the colour industry.

F. M. G. M.

Preparation of Dibromophenylglycine-*o*-carboxylic Acid. Aktiengesellschaft für Anilinfabrikation (D.R.-P. 216266).—Bromophenylglycine-*o*-carboxylic acid has previously been prepared by the action of bromine on phenylglycine-*o*-carboxylic acid in either mineral or acetic acid, or organic solvents. A *dibromophenylglycine-o-carboxylic acid* is produced when phenylglycine-*o*-carboxylic acid (19·5 parts), dissolved in 50% sulphuric acid, is kept at 30° and constantly agitated whilst bromine vapour (32 parts) is introduced with a current of air. The crude product is dissolved in the calculated amount of alkali, reprecipitated with hydrochloric acid, and warmed, when it becomes converted into a colourless, crystalline powder, insoluble in water, but soluble in alcohol or acetic acid, m. p. 227—228° (decomp.). That the bromine has entered the phenyl ring is shown by the non-formation of sodium bromide when the substance is boiled with sodium ethoxide.

F. M. G. M.

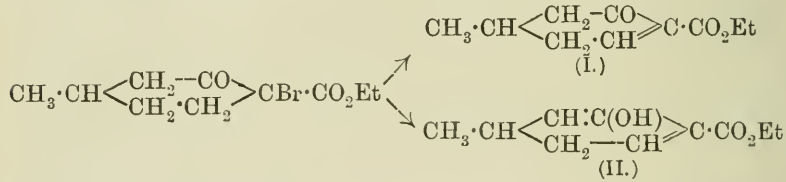
Syntheses Effected by Phenylacetonitrile. F. Bodroux and Felix Taboury (*Compt. rend.*, 1910, 150, 531—533).—The sodium derivatives of nitriles of the type R·CHNa·CN, prepared by treating the nitriles in ethereal solution with sodamide, readily undergo condensation with alkyl halides; thus ethyl iodide reacts with the sodium derivative of phenylacetonitrile, forming α-phenylbutyronitrile (Neure, Abstr., 1889, 597). *α-Phenyl-β-methylbutyronitrile*, $CHPr^{\beta}Ph{\cdot}CN$, has b. p. 245—249°/765 mm.; $D^{15\cdot5}$ 0·967; on hydrolysis it forms *α-phenyl-β-methyl-n-butyramide*, $CHPr^{\beta}Ph{\cdot}CO{\cdot}NH_2$, silky needles, m. p. 111—112°. *α-Phenyl-γ-methylvaleronitrile*, $C_{12}H_{15}N$, has b. p. 263—266°/765 mm.; D_{16} 0·942. When hydrolysed it yields *α-phenyl-γ-methylvaleric acid*, prisms, m. p. 78—79°.

W. O. W.

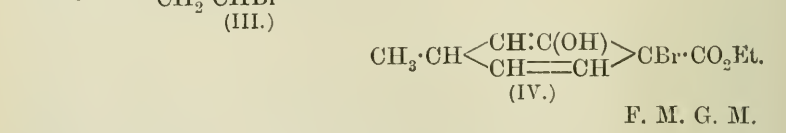
Acids of the Phenylpropiolic Series and their Condensation to Naphthalene Derivatives. John E. Bucher (*J. Amer. Chem. Soc.*, 1910, 32, 212—221).—A review of work done in connexion with phenylpropiolic acid and its derivatives, with special reference to that of the author and his collaborators (compare Michael and Bucher, Abstr., 1896, i, 85; 1898, i, 256; Bucher, Abstr., 1908, i, 791; Bucher and Slade, this vol., i, 38). E. G.

Preparation of Di- and Tetra-hydro-β-ketonic Acids or their Esters. Arthur Kötz (D.R.-P. 215424).—When the halogen derivatives of hydroaromatic-β-ketonic-carboxylic acid esters are treated with agents for removing halogen, or distilled under atmospheric pressure, hydrogen halide is eliminated, and unsaturated compounds, many of which are of therapeutic value, are produced. The preparation and properties of 2-bromo*cyclo*hexanone, Δ^2-*cyclo*hexenone and its semicarbazone, and of ethyl-2-hydroxy-$\Delta^{2:6}$-*cyclo*hexadienecarboxylate from ethyl bromo-1-*cyclo*hexanone-2-carboxylate are described (compare Abstr., 1908, i, 173).

Ethyl 4-bromo-1-methyl-3-*cyclo*hexanone-4-carboxylate on distillation yields *ethyl* 1-*methyl*-Δ^3-cyclo*hexen*-5-*one*-4-*carboxylate* (I), a yellow oil, b. p. 110°/15 mm., or its enolic form, *ethyl* 1-*methyl*-$\Delta^{2:4}$-*hexadiene*-3-*ol*-4-*carboxylate* (II), the bromination of which with



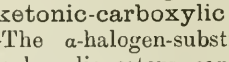
2 atoms of bromine in carbon disulphide solution leads to the formation of ethyl 4 : 5-dibromo-1-methyl-Δ^2-*cyclo*hexene-3-ol-4-carboxylate (III); this on distillation gives *ethyl bromo*-1-*methyl*-$\Delta^{2,5}$-cyclo*hexadiene*-3-*ol*-4-*carboxylate* (IV), a pale yellow oil, b. p. 161°/13 mm.:



F. M. G. M.

Preparation of α-Monohalogen-substitution Products of Hydroaromatic-β-ketonic-carboxylic Esters. Arthur Kötz (D.R.-P. 215423).—The α-halogen-substitution products of hydroaromatic-β-ketonic carboxylic esters can be obtained by the direct halogenation of these substances.

Ethyl 1-*chloro*-2-cyclo*hexanone*-1-*carboxylate*,



b. p. 138—139°/13 mm., an oily fluid with penetrating odour, is

obtained when ethyl 2-*cyclo*hexanone-1-carboxylate is cooled and treated with dry chlorine; hydrogen chloride is removed by a current of dry carbon dioxide, and the product distilled under reduced pressure.

Ethyl 1-*bromo*-2-cyclo*hexanone*-1-*carboxylate* is similarly prepared by employing bromine instead of chlorine, as in the previous experiment; it is a pale yellow oil with unpleasant odour, and has b. p. 144°/13 mm.

Ethyl 4-*chloro*-1-*methyl*-3-cyclo*hexanone*-4-*carboxylate*,

$$CH_3\cdot CH<\begin{matrix}CH_2\text{---}CO\\CH_2\cdot CH_2\end{matrix}>CCl\cdot CO_2Et,$$

b. p. 138°/11 mm., is obtained from ethyl 1-methyl-3-*cyclo*hexanone-4-carboxylate, but the action proceeds with less violence.

Ethyl 1-*bromo*-1-*methyl*-3-cyclo*hexanone*-4-*carboxylate*, b. p. 149—150°/12 mm., has similar properties, but in this case the reaction does not proceed readily unless hydrogen bromide is expelled by shaking during the experiment. F. M. G. M.

Some Derivatives of Salicylic Acid. Alfred Einhorn and Alexander von Bagh (*Ber.*, 1910, 43, 322—336).—o-4-*Nitrobenzoyloxybenzoic acid*, $CO_2H\cdot C_6H_4\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, m. p. 205°, is a yellow, crystalline powder obtained by adding a benzene solution of *p*-nitrobenzoyl chloride to a well cooled solution of salicylic acid and dimethylaniline in the same solvent. The *ethyl* ester,

$$CO_2Et\cdot C_6H_4\cdot O\cdot CO\cdot C_6H_4\cdot NO_2,$$

m. p. 107—108°, prepared from ethyl salicylate and *p*-nitrobenzoyl chloride in pyridine, is reduced by stannous chloride and alcoholic hydrogen chloride to *ethyl* o-4-*aminobenzoyloxybenzoate*, m. p. 109—110°. *Ethyl* o-4-*dimethylaminobenzoyloxybenzoate*, m. p. 106°, is obtained by heating ethyl salicylate and *p*-dimethylaminobenzoic anhydride for ten hours at 180—200°. The *chlorocarbonate* of methyl salicylate, $CO_2Me\cdot C_6H_4\cdot O\cdot COCl$, m. p. 24°, b. p. 141—142°/0 mm., is ultimately obtained when a cooled 20% benzene solution of carbonyl chloride is slowly added to methyl salicylate and quinoline dissolved in benzene; its ethereal solution yields with ethereal ammonia the *carbamate*, $CO_2Me\cdot C_6H_4\cdot O\cdot CO\cdot NH_2$, m. p. 145°, and with ethereal diethylamine the *diethylcarbamate*, b. p. 182°/0 mm. The passing of hydrogen chloride into a well-cooled suspension of the carbamate in 40% formaldehyde leads to the formation of the *dichlorodimethylcarbamate*,

$$CO_2Me\cdot C_6H_4\cdot O\cdot CO\cdot N(CH_2Cl)_2,$$

m. p. 75—76°, a cold ethereal solution of which reacts with piperidine to form methyl salicylate, formaldehyde, and *α-piperidyl-β-*(1)*-piperidylmethylcarbamide*, $C_5NH_{10}\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10}$, m. p. 142—143°.

o-*Carbomethoxyphenyl* m-*carbethoxyphenylcarbamate*,

$$CO_2Me\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Et,$$

m. p. 123°, is obtained by slowly mixing cold ethereal solutions of the chlorocarbonate of methyl salicylate and ethyl *m*-aminobenzoate. The corresponding *para*-compound, m. p. 153—154°, prepared in a similar manner, loses methyl alcohol after some hours at 130—140°, and

yields the *ethyl carbonylsalicyl*-p-*aminobenzoate*, m. p. 185—187°, described below.

o-*Ethylcarbonatobenzoyl chloride*, $COCl\cdot C_6H_4\cdot O\cdot CO_2Et$, b. p. 155—165°/20—25 mm., obtained by the action of phosphorus pentachloride on *o*-ethylcarbonatobenzoic acid (Abstr., 1909, i, 161) in chloroform, reacts with methyl anthranilate in cold pyridine to form *methyl* o-*ethylcarbonatobenzoylanthranilate*,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Me,$$

m. p. 113°, which loses ethyl alcohol at 230°, forming *methyl carbonylsalicyl*-o-*aminobenzoate*, $CO_2Me\cdot C_6H_4\cdot N<\begin{matrix}CO\cdot O\\CO\end{matrix}>C_6H_4$, m. p. 145°.

o-Ethylcarbonatobenzoyl chloride reacts with ethyl *m*-aminobenzoate in cold pyridine directly to form *ethyl carbonylsalicyl*-m-*aminobenzoate*, m. p. 185—186°, and similarly with ethyl *p*-aminobenzoate to form *ethyl carbonylsalicyl*-p-*aminobenzoate*, m. p. 185—187°. *Ethyl* o-*ethylcarbonatobenzoyl*-p-*aminobenzoate*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot O\cdot CO_2Et$, m. p. 90—92°, is obtained, however, when an ethereal solution of ethyl *p*-aminobenzoate is treated with *o*-ethyl carbonatobenzoyl chloride at 0°; it is converted into the preceding compound at 160—200°. o-*Ethylcarbonatobenzoic anhydride*, $O(CO\cdot C_6H_4\cdot O\cdot CO_2Et)_2$, m. p. 62—64°, is obtained from salicylic acid diethyl dicarbonate (D.R.-P. 117267) by prolonged keeping, and is converted by cold concentrated ammonium hydroxide into *carbonylsalicylamide*, m. p. 227°. C. S.

Colourless and Yellow Thiosalicylic [*o*-Thiolbenzoic] Acids. Oscar Hinsberg (*Ber.*, 1910, 43, 651—654).—*o*-Thiolbenzoic acid, $SH\cdot C_6H_4\cdot CO_2H$, exists in a colourless as well as in the ordinary yellow modification, whereas its methyl and acetyl derivatives have been obtained in colourless modifications only. Other thiophenols also exist in two modifications (Abstr., 1906, i, 654).

α-o-Thiolbenzoic acid, obtained by treating the crude acid or dithiosalicylic acid (m. p. 289°) with glacial acetic acid, tin, and concentrated hydrochloric acid until all is dissolved, crystallises in colourless prisms, m. p. 164—165°. It is less soluble than the yellow isomeride, from which it is obtained by treatment with stannous chloride and glacial acetic acid or by heating at 200°. The yellow isomeride, *β-o*-thiolbenzoic acid, has m. p. 163—164°, after softening at 158°.

The *methyl ether*, $SMe\cdot C_6H_4\cdot CO_2H$, crystallises in long, colourless needles, m. p. 169°, and undergoes no alteration when heated to 250°. o-*Acetylthiolbenzoic acid*, $SAc\cdot C_6H_4\cdot CO_2H$, crystallises in colourless needles, m. p. 125°, and when hydrolysed with hydrochloric acid yields *α-o*-thiolbenzoic acid. J. J. S.

Derivatives of Thiosalicylic [*o*-Thiolbenzoic] Acid and of Thioxanthone. Fritz Mayer (*Ber.*, 1910, 43, 584—596. Compare Abstr., 1909, i, 405, 823).—Methyl, carboxy-, polynitro-, and chloronitro-derivatives of thiosalicylic [*o*-thiolbenzoic] acid have been prepared, mainly by heating substituted benzoic acids with thiosalicylic acid and copper powder under pressure.

The products can be oxidised in much the same manner as the compounds already described, but it is found that 2 : 2′-thiodibenzoic acid,

like other ortho-compounds, is completely destroyed by chromic acid; the ester, on the other hand, is readily oxidised to a sulphoxide ester. Dinitro-2 : 2′-thiodibenzoic acid is only slowly oxidised by chromic anhydride in acetic acid solution, and the *s*-trinitro-derivative is extremely resistant to oxidising agents (Blanksma, *Rec. trav. chim.*, 1901, 20, 426).

Most of the sulphides can be transformed into thioxanthones by means of sulphuric acid. The dinitro-derivative does not yield a thioxanthone by this method, but the corresponding amino-compound does. When the acid chloride of dinitrothiodibenzoic acid is heated with aluminium chloride and nitrobenzene, it yields 2 : 4-dinitrothioxanthone, but with benzene and aluminium chloride yields 2 : 4-dinitro-2′-benzoyldiphenyl sulphide.

The thioxanthonecarboxylic acids readily loses carbon dioxide, yielding thioxanthones.

4-Methyl-2′-carboxydiphenyl sulphide [2 : 2′-thio-4-methyldibenzoic acid] (compare Goldberg, Abstr., 1905, i, 59) can be prepared by condensing *o*-diazobenzoic acid with an alkaline solution of *p*-thiocresol.

The corresponding *sulphoxide*, $C_6H_4Me\cdot SO\cdot C_6H_4\cdot CO_2H$, crystallises in colourless needles, and has m. p. 244°, after softening at 236°.

2-Methylthioxanthone, $C_6H_4\langle{}^{S}_{CO}\rangle C_6H_3Me$, crystallises in yellow needles, m. p. 123°, and when oxidised with chromic anhydride yields 2-methylbenzophenonesulphone (Ullmann and Lehner, Abstr., 1905, i, 290).

2 : 2′-*Dicarboxydiphenyl sulphide* [2 : 2′-*thiodibenzoic acid*],

$$S(C_6H_4\cdot CO_2H)_2,$$

obtained by heating thiosalicylic acid, *o*-chlorobenzoic acid, copper powder, potassium carbonate, and water at 135—140° for three hours, crystallises in colourless needles, m. p. 229—230°. The *methyl* ester, $C_{16}H_{14}O_4S$, has m. p. 84°, and the *ethyl* ester, $C_{18}H_{18}O_4S$, m. p. 57—58°.

2 : 2′-*Dicarboxydiphenyl sulphoxide* [*sulphonyldibenzoic acid*],

$$O{:}S(C_6H_4\cdot CO_2H)_2,$$

is best obtained by hydrolysis of its esters, and crystallises in well developed, colourless prisms, m. p. 312°. The *methyl* ester, $C_{16}H_{14}O_5S$, crystallises in brilliant plates, m. p. 156°, and the *ethyl* ester,

$$C_{18}H_{18}O_5S,$$

in compact needles, m. p. 107—108°. 2 : 2′-*Dicarboxydiphenylsulphone*, $SO_2(C_6H_4\cdot CO_2H)_2$, obtained by oxidising the sulphide with permanganate, crystallises in felted needles, m. p. 138—139°. *Thioxanthone-4-carboxylic acid*, $C_6H_4\langle{}^{S}_{CO}\rangle C_6H_3\cdot CO_2H$, forms yellow, microscopic crystals, m. p. 336—337°. The *methyl* ester, $C_{15}H_{10}O_3S$, has m. p. 191°, and the *amide*, $C_{14}H_9O_2NS$, forms pale yellow needles, m. p. 286°.

o-2′ : 4′-*Dinitrophenylthiolbenzoic acid*, $C_6H_3(NO_2)_2\cdot S\cdot C_6H_4\cdot CO_2H$, obtained from 1-chloro-2 : 4-dinitrobenzene, forms yellow crystals, m. p. 179—180°; the *methyl* ester has m. p. 117—117·5°; the *sulphoxide*, $C_{12}H_8O_7N_2S$, forms compact, pale greenish-yellow crystals, m. p. 239—240°, and yields a *methyl* ester, $C_{14}H_{10}O_7N_2S$, m. p. 171—172°;

the *sulphone*, $C_{13}H_8O_8N_2S$, forms colourless crystals, m. p. 215—217°; 2 : 4-*dinitro*-2′-*benzoyldiphenyl sulphide*, $C_6H_3(NO_2)_2\cdot S\cdot C_6H_4\cdot COPh$, has m. p. 155—156°, and the corresponding *toluoyl* derivative,

$$(NO_2)_2C_6H_3\cdot S\cdot C_6H_4\cdot CO\cdot C_6H_4Me,$$

has m. p. 122°. 2 : 4-*Dinitrothioxanthone*, $C_6H_4<\begin{matrix}S\\CO\end{matrix}>C_6H_2(NO_2)_2$, forms greenish-yellow needles with a metallic lustre, and has m. p. 225—226°.

o-2′ : 4′ : 6′-*Trinitrophenylthiolbenzoic acid*, $(NO_2)_3C_6H_2\cdot S\cdot C_6H_4\cdot CO_2H$, obtained from picryl chloride, forms yellow crystals, m. p. 240—241°. The *methyl* ester forms brilliant, reddish-yellow needles, m. p. 181·5°.

o-4′-*Chloro*-2′-*nitrophenylthiolbenzoic acid*,

$$NO_2\cdot C_6H_3Cl\cdot S\cdot C_6H_4\cdot CO_2H,$$

has m. p. 155—156·5°, and 2-*chloro*-4-*nitrothioxanthone*,

$$C_6H_4<\begin{matrix}S\\CO\end{matrix}>C_6H_2Cl\cdot NO_2,$$

forms slender, yellow needles, m. p. 219—220°.

o-5-*Chloro*-2-*nitrophenylthiolbenzoic acid*, $C_{13}H_8O_4NClS$, obtained from 1-chloro-3 : 4-dinitrobenzene, has m. p. 188—189°, and 1-*chloro*-4-*nitrothioxanthone*, $C_{13}H_6O_3NClS$, m. p. 204—205°. J. J. S.

Action of Sulphosalicylic Acid on Trisodium Phosphate. Léonce Barthe (*Compt. rend.*, 1910, **150**, 401—403. Compare Abstr., 1908, i, 271).—*Sodium oxyphosphodisulphosalicylate*,

$$PO[O\cdot C_6H_3(SO_3H)\cdot CO_2Na]_2\cdot ONa,$$

is obtained in the form of brilliant prisms containing $2H_2O$ when a boiling aqueous solution of trisodium phosphate is mixed with an alcoholic solution of sulphosalicylic acid. The compound is a dibasic acid; it gives a red coloration with Millon's reagent, and a bluish-violet colour with ferric chloride.

By the interaction of trisodium arsenate and sulphosalicylic acid, a *compound* has been obtained, the composition of which appears to agree with the formula $AsO[O\cdot C_6H_3(SO_3H)\cdot CO_2Na]_3$.

W. O. W.

Preparation of *o*- and *peri*-Thiophenolcarboxylic Acids. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 216269).—*o*- or *peri*-Cyanoarylsulphinic acids are obtained in the form of their zinc salts by the slow reduction at the ordinary temperature of cyanoarylsulphonyl chlorides with zinc dust and water; the free acids are colourless powders, sparingly soluble in water, without characteristic melting point, and readily undergo atmospheric oxidation to the corresponding sulphonic acids. The zinc salts are somewhat sparingly soluble in water. When the preceding reduction mixture is treated with sulphuric acid and a further quantity of zinc, and the action allowed to proceed during several days until the evolution of nitrogen ceases, the corresponding zinc thiophenolcarboxylates are precipitated, the hydrolysis of the nitrile group having taken place simultaneously with the reduction of the sulphinic group. These acids are colourless, crystalline powders, soluble in alkali carbonates, yielding characteristic colours with concentrated sulphuric acid, and are readily oxidised to the corresponding dithio-acids.

5-Chloro-3-thiol-*o*-toluic acid, $SH\cdot C_6H_2MeCl\cdot CO_2H$, m. p. about 235°, is prepared by treating diazotised 5-chloro-*o*-toluidine-3-sulphinic acid with cuprous cyanide, and the 2-cyanotoluene-3-sulphinic acid then formed, with phosphorus pentachloride, and subsequently reducing first with zinc dust in acetone solution, and, finally, in the presence of sulphuric acid; it forms colourless needles, yields a blue coloration with concentrated sulphuric acid, and is readily oxidised to dithiochlorotoluic acid. The following compounds are mentioned in the patent:

3-*Thiol*-p-*toluic acid*, $SH\cdot C_6H_3Me\cdot CO_2H$, prepared from the corresponding cyanotoluenesulphinic acid.

6-*Thiol*-2 : 4-*dimethylbenzoic acid*, $SH\cdot C_6H_2Me_2\cdot CO_2H$, from cyanoxylenesulphinic acid.

2-*Thiolnaphthalene*-1-*carboxylic acid*, $SH\cdot C_{10}H_6\cdot CO_2H$, from 1-cyanonaphthalene-2-sulphinic acid; and 8-*thiolnaphthalene*-1-*carboxylic acid*, from the corresponding 1 : 8-cyanosulphinic acid.

F. M. G. M.

Methyl Anisoylacetates. André Wahl and C. Silberzweig (*Compt. rend.*, 1910, 150, 538—540. Compare Abstr., 1908, i, 647).—The three methyl anisoylacetates have been prepared by condensing methyl acetate with *o*-, *m*-, and *p*-methoxybenzoic acids in presence of sodium.

Methyl o-*anisoylacetate*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2Me$, is a pale yellow liquid boiling at 179—180°/15 mm., with formation of small quantities of o-*anisoyldehydracetic acid*, occurring in yellow crystals, m. p. 214—215°. The green *copper* salt, $(C_{10}H_{11}O_4)_2Cu$, has m. p. 170—172°; a solution in methyl alcohol deposits, on boiling, blue crystals of a basic salt, $C_{12}H_{14}O_5Cu$ (compare Wislicenus, Abstr., 1899, i, 192). The following derivatives of the new ester are described: the *nitroso*-derivative, m. p. 145—147°; o-*anisoylphenylpyrazolone*, m. p. 133—134°; o-*anisoyl*-p-*nitrophenylpyrazolone*, m. p. 217—218°; *methyl benzeneazo*-o-*anisoylacetate*, m. p. 138—139°.

Methyl m-*anisoylacetate* is an amber-coloured liquid, b. p. 180°/14 mm., forming a green *copper* salt, m. p. 172—173°, and a *nitroso*-derivative, m. p. 115—116°. m-*Anisoyldehydracetic acid* occurs in yellow crystals, m. p. 185°. m-*Anisoylphenylpyrazolone* has m. p. 124°; *methyl benzeneazo*-m-*anisoylacetate* has m. p. 72—73°.

Methyl p-*anisoylacetate* forms pale yellow crystals, m. p. 27—28°, b. p. 190—192°/10 mm. The *copper* salt has m. p. 248—250°, and the *nitroso*-derivative, m. p. 154°. p-*Anisoyldehydracetic acid* has m. p. 190°; p-*anisoylphenylpyrazolone* has m. p. 136—137°. *Methyl benzeneazo*-p-*anisoylacetate*, m. p. 121—122°, forms an *acetyl* derivative, m. p. 111—113°; as this yields acetanilide on reduction, it would appear to be an acetylhydrazone (compare Schoonjans, Abstr., 1898, i, 425). W. O. W.

Action of Amines on Phthalic Acid. VI. J. Bishop Tingle an B. F. Parlett Brenton (*J. Amer. Chem. Soc.*, 1910, 32, 113—117).—A study has been made of the action of phthalic anhydride on several amino-compounds. With camphylamine, *phthalylcamphylimide*,

$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_{10}H_7$, m. p. 54°, is produced. In the case of benzidine, an insoluble compound is obtained, which does not melt below 300°. *m*-Aminobenzoic acid yields phthalyl-*m*-aminobenzoic acid, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$ (compare Gabriel, Abstr., 1879, 323, and Piutti, Abstr., 1883, 999).

Acetanilide, aceto-*p*-toluidide, and formo-*β*-naphthalide react with phthalic anhydride with the replacement of the acetyl or formyl group by the phthalyl group, phthalyl-*β*-naphthylimide, for example, being produced from formo-*β*-naphthalide. Carbamide, methylcarbamide, ethylcarbamide, benzylcarbamide, and phenylcarbamide are converted into phthalimide, methylphthalimide, ethylphthalimide, benzylphthalimide, and phenylphthalimide respectively, ammonia and carbon dioxide being evolved in each case. Phenylthiocarbamide behaves in the same way as phenylcarbamide, except that carbonyl sulphide is evolved instead of carbon dioxide. E. G.

Action of Unsaturated Dicarboxylic Acids on *p*-Aminophenols. Arnaldo Piutti (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], **15**, 315—318).—A résumé is given of the work of the author and his assistants on the amic acids, imides, and diamides derived from the actions of maleic, fumaric, citraconic, mesaconic, itaconic, pyrocinchonic, phthalic, and camphoric acids on various *p*-aminophenols (compare this vol., i, 22). The cases of chromo-isomerism and of true chemical isomerism observed with these compounds are indicated. T. H. P.

New Synthesis of 4:4′-Dimethylpyranthrone. Roland Scholl, Kurt Liese, Karl Michelson, and Ernst Grunewald (*Ber.*, 1910, **43**, 512—518. Compare this vol., i, 271).—The reaction in carbon disulphide between 2:4:2′:4′-tetramethyl-1:1′-diphenyl, phthalic anhydride, and aluminium chloride leads to the formation of a tarry product containing at least three substances. The residue left by treating the product with a large volume of cold benzene is crystallised from chloroform, and consists of 2:4:2′:4′-*tetramethyldiphenyl*-5:5′-*diphthaloylic acid*, $C_{12}H_4Me_4(CO\cdot C_6H_4\cdot CO_2H)_2$, m. p. 242°, the constitution of which is proved by its conversion by concentrated sulphuric acid into 2:4:2′:4′-tetramethyl-1:1′-dianthraquinoyl, which in turn was converted into 4:4′-dimethylpyranthrone. The benzene extract of the tarry product is evaporated, and the residue is separated by ether and by cold chloroform into two substances, the one soluble, the other insoluble. The latter is recrystallised from nitrobenzene, and consists probably of 2:4:2′:4′-*tetramethyldiphenyl*-3:3′-*diphthaloylic acid*, m. p. 320°, since it is converted by concentrated sulphuric acid, not into an anthraquinone derivative, but into a *disulphonic acid*, $C_{32}H_{26}O_{12}S_2$. The soluble substance has not been obtained pure. It has m. p. 92—94°, and appears to have the composition $C_{32}H_{24}O_5$; it is not an anthraquinone derivative, and is not converted into one by concentrated sulphuric acid at 120°, is soluble in dilute alkali, and is provisionally regarded as 2:4:2′:4′-*tetramethyl*-5:5′-*phthaloyldiphenyl*-3-*phthaloylic acid*. C. S.

Constitution of Tannin. VII. Maximilian Nierenstein (*Ber.*, 1910, **43**, 628—634. Compare Abstr., 1906, i, 446; 1907, i, 331; 1908, i, 80, 897; 1909, i, 402, 948).—The following facts are brought forward in favour of the view that pure tannin is a mixture of a digallic acid and leucotannin. By repeated conversion into its ethyl carbonato-derivative and hydrolysis of this with pyridine (Fischer, Abstr., 1908, i, 892), it has been found possible to isolate digallic acid in a crystalline, optically inactive form.

d-l-Hexa-acetyl-leucotannin can be obtained by the reduction of penta-acetyldigallic acid with zinc dust and acetic acid in the presence of acetic anhydride, and is readily resolved into its optically active components by means of strychnine. Both acetyl compounds can be hydrolysed by means of sodium carbonate solution saturated with carbon dioxide.

The view that the activity of tannin is due to the leucotannin and not to the presence of a sugar (Abstr., 1909, i, 174) is still held.

Digallic acid, $C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)_2\cdot CO_2H$, crystallises with $2H_2O$, which it loses at 110°, and then has m. p. 268—270°, after sintering at 214°. It is inactive, and when oxidised with hydrogen peroxide yields luteoic and ellagic acids (Abstr., 1908, i, 897). The *penta-acetyl* derivative, $C_{24}H_{20}O_{14}$, crystallises in slender needles, m. p. 211—214°, and the *pentabenzoyl* derivative, $C_{49}H_{30}O_{14}$, has m. p. 187—189°. The *pentaethylcarbonato*-compound,

$$C_6H_2(O\cdot CO_2Et)_3\cdot CO\cdot O\cdot C_6H_2(O\cdot CO_2Et)_2\cdot CO_2H,$$

crystallises in small cubes, m. p. 194—195°.

d-l-*Hexa-acetyl-leucotannin*,

$$C_6H_2(OAc)_3\cdot CH(OAc)\cdot O\cdot C_6H_2(OAc)_2\cdot CO_2H,$$

also crystallises in small cubes, m. p. 154—155°.

Strychnine l-hexa-acetyl-leucotannin is less soluble than the *d*-salt, and *l*-hexa-acetyl-leucotannin itself crystallises in minute needles containing $1H_2O$ and having m. p. 151° and $[\alpha]_D^{15}$ −46°. The *d*-compound has m. p. 153—154° and $[\alpha]_D^{20}$ +121·5°.

The digallic acid is not identical with Fischer's acid. J. J. S.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. IV. Emil Fischer and Karl Freudenberg (*Annalen*, 1910, **372**, 32—68. Compare Fischer, Abstr., 1908, i, 892; 1909, i, 161, 309).—The present communication contains a description of the syntheses of many complex substances which have been effected by coupling the sodium salts of phenolcarboxylic acids with the chlorides of methylcarbonato-carboxylic acids; for example, *p*-ethylcarbonatobenzoyl-*p*-oxybenzoyl chloride reacts with sodium *p*-hydroxybenzoyl-*p*-oxybenzoate, yielding the ethylcarbonato-derivative of tri-*p*-oxybenzoyl-*p*-oxybenzoic acid,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

which when hydrolysed cautiously yields the corresponding phenolcarboxylic acid; di-*p*-oxybenzoyl-*p*-oxybenzoic acid,

$$OH\cdot[C_6H_4\cdot CO\cdot O\cdot]_2\cdot C_6H_4\cdot CO_2H,$$

is similarly prepared from *p*-ethylcarbonatobenzoyl chloride and *p*-hydroxybenzoyl-*p*-oxybenzoic acid. It will no doubt be possible to prepare, by similar means, a large number of analogous substances from

other hydroxybenzoic acids, and since many undoubtedly occur in nature, as, for example, tannin, it is considered advisable to classify them under the collective name *depside* (δέψειν tan), and, as in the case of the polysaccharides and polypeptides, to distinguish between di-, tri-, tetra-depsides, etc., according to the number of phenolcarboxylic acid residues contained in the molecule.

The preparation and properties of vanilloylvanillin and vanilloylglycine are described, likewise a method whereby a 45% yield of *p*-hydroxybenzoyloxybenzoic acid may be obtained by acting on an ethereal solution of *p*-hydroxybenzoic acid with phosphoryl chloride.

p-*Ethylcarbonatobenzoic acid*, $CO_2Et\cdot O\cdot C_6H_4\cdot CO_2H$, prepared from *p*-hydroxybenzoic acid and ethyl chlorocarbonate, crystallises in long, colourless needles, m. p. 156—157° (corr.); the *chloride*, $C_{10}H_9O_4Cl$, has m. p. 41°, b. p. 170°/12 mm. The latter substance interacts with *p*-hydroxybenzoyl-*p*-oxybenzoic acid in an aqueous solution of sodium hydroxide, yielding *ethylcarbonatodi*-p-*oxybenzoyl*-p-*oxybenzoic acid*,

$$C_{24}H_{18}O_9,$$

which crystallises from amyl alcohol in aggregates of colourless leaflets and from pyridine in small, slender needles, m. p. 243—244° (corr., decomp.), and when hydrolysed cautiously yields *di*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{21}H_{14}O_7$, which crystallises in long, colourless needles, commences to decompose at 283° (corr.), fuses at 300° (corr.), and is probably identical with the compound obtained by Klepl by strongly heating *p*-hydroxybenzoic acid (compare Abstr., 1884, 446).

p-*Ethylcarbonatobenzoyloxybenzoic acid*, $C_{17}H_{14}O_7$, obtained by the action of *p*-ethylcarbonatobenzoyl chloride on *p*-hydroxybenzoic acid, crystallises in colourless leaflets, m. p. 112° (corr.); the *chloride*, $C_{17}H_{13}O_6Cl$, crystallises in small, slender needles, m. p. 113° (corr.), and couples with *p*-hydroxybenzoyloxybenzoic acid, yielding *ethylcarbonatotri*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{31}H_{22}O_{11}$, which crystallises from acetylene tetrachloride in stellate aggregates of microscopic, slender leaflets, m. p. 275° (corr., decomp.), and on partial hydrolysis yields *tri*-p-*oxybenzoyl*-p-*oxybenzoic acid*,

$$OH\cdot[C_6H_4\cdot CO\cdot O\cdot]_3C_6H_4\cdot CO_2H,$$

crystallising from ethyl oxalate in microscopic, colourless, silky needles, m. p. 325° (corr., decomp.); the tetradepside is extremely insoluble in organic solvents, and is not identical with Schiff's tetra-*p*-oxybenzoid (compare Abstr., 1883, 335).

4-*Methylcarbonato*-3-*methoxybenzoic acid*,

$$CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CO_2H,$$

is prepared by the interaction of vanillic acid and methyl chlorocarbonate in a *N*-sodium hydroxide solution; it crystallises in small, colourless needles, m. p. 159° (corr., decomp.), and may be sublimed in a current of carbon dioxide at 145—150°; it does not give a coloration with ferric chloride, although, contrary to Tiemann's statement (compare Abstr., 1875, 1198), vanillic acid gives an intense reddish-brown coloration; the *chloride*, $C_{10}H_9O_5Cl$, crystallises in small, colourless needles, m. p. 79°, b. p. 180°(corr.)/11 mm., and interacts (1) with *p*-hydroxybenzoic acid, yielding 4-*methylcarbonato*-3-*methoxybenzoyl*-p-*oxybenzoic acid*, $CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, colourless, microscopic leaflets, m. p. 219° (corr., decomp.), which is hydrolysed

by a cold *N*-solution of ammonium hydroxide, yielding *vanilloyl*-p-*oxybenzoic acid*, $OH\cdot C_6H_3(OMe)\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, small needles, prisms, and leaflets, m. p. 227° (corr.); (2) with *p*-hydroxybenzoyloxybenzoic acid, yielding 4-*methylcarbonato*-3-*methoxybenzoyl*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{24}H_{18}O_{10}$, glistening, slender leaflets and needles, m. p. 244—246° (corr.), the *chloride* of which, $C_{24}H_{17}OCl$, crystallises in microscopic leaflets, m. p. 170—171 (corr.); the former compound when hydrolysed yields *vanilloyl*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{22}H_{16}O_8$, m. p. 241° (corr.), crystallising with 1Me·OH in long, slender prisms; (3) with vanillin, yielding 4-*methylcarbonato*-3-*methoxybenzoylvanillin*, $C_{18}H_{16}O_8$, and is converted by a dilute aqueous methyl-alcoholic solution of sodium hydroxide into *vanilloylvanillin*,

$$OH\cdot C_6H_3(OMe)\cdot CO_2\cdot C_6H_3(OMe)\cdot CHO,$$

crystallising in tufts of colourless, glistening needles, m. p. 140—141° (corr.), the sodium hydrogen sulphite *compound* of which forms slender, colourless needles; (4) with ethyl aminoacetate, yielding *ethyl* 4-*methylcarbonato*-3-*methoxybenzoylaminoacetate*, $C_{14}H_{17}O_7N$, which crystallises in glistening, four-sided leaflets, m. p. 93—94° (corr.), and on hydrolysis yields *vanilloylglycine*, $OH\cdot C_6H_3(OMe)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, short, microscopic prisms, m. p. 167°; the latter substance crystallises with H_2O in large, colourless leaflets, which sinter at about 75°; it has both an acid and bitter taste.

4-*Methylcarbonato*-3-*methoxybenzoyl*-p-*oxybenzoyl chloride*, $C_{17}H_{13}O_7Cl$, crystallises in microscopic leaflets and needles, m p. 128—129° (corr.), and reacts with *p*-hydroxybenzoyloxybenzoic acid, yielding 4-*methylcarbonato*-3-*methoxybenzoyldi*-p-*oxybenzoyl*-p-*oxybenzoic acid*,

$$CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CO_2\cdot[C_6H_4\cdot CO\cdot O\cdot]_2C_6H_4\cdot CO_2H,$$

which crystallises in stellate groups of small leaflets, m. p. 272° (corr., decomp.), and when hydrolysed yields *vanilloyldi*-p-*oxybenzoyl*-p-*oxybenzoic acid*, crystallising in small needles and microscopic, spear-shaped plates, m. p. 254° (corr., decomp.).

4-*Methylcarbonato*-3-*methoxybenzaldehyde*, $C_{10}H_{10}O_5$, prepared from vanillin and methyl chlorocarbonate, forms colourless needles, m. p. 89° (corr.); it yields the corresponding acid when oxidised with potassium permanganate, which readily passes into vanillic acid. W. H. G.

Photochemistry of *o*-Nitrated Benzaldehydes. Eugen Bamberger and Franz Elgar (*Annalen*, 1910, 371, 319—365).—The formation of ethyl *o*-nitrosobenzoate by the action of light on an ethyl-alcoholic solution of *o*-nitrobenzaldehyde (compare Ciamician and Silber, Abstr., 1901, i, 390; 1902, i, 433) is shown to take place in the following stages: $NO_2\cdot C_6H_4\cdot CHO \xrightarrow{Et\cdot OH} NO_2\cdot C_6H_4\cdot CH(OEt)_2 \longrightarrow [NO\cdot C_6H_4\cdot C(OEt)_2\cdot OH] \longrightarrow NO\cdot C_6H_4\cdot CO_2Et + Et\cdot OH$; it has been found possible to isolate the *o*-nitrobenzaldehydediethylacetal formed in this way. A second reaction takes place simultaneously, namely, the formation of 2:2′-azoxybenzoic acid by way of *o*-nitrosobenzoic acid. Methyl alcohol, propyl alcohol, *iso*propyl alcohol, and *iso*butyl alcohol react in the same way as ethyl alcohol; in the case of *iso*propyl alcohol, however, only a very small quantity of *iso*propyl *o*-nitroso-benzoate is formed, the chief product being *o*-nitrosobenzoic acid; this is found to be due to the slow rate with which the *iso*propyl-

acetal of *o*-nitrobenzaldehyde is formed, for the latter substance decomposes into *iso*propyl *o*-nitrosobenzoate and *iso*propyl alcohol under the influence of light with almost the same readiness with which the other acetals undergo the analogous transformation.

Quantitative experiments carried out with the alcohols mentioned show that the rate with which the acetal is formed, either through the agency of sunlight or by using hydrogen chloride as a catalyst, decreases as the mol. wt. of the alcohol increases, except with *iso*propyl alcohol, when the quantity of acetal formed in a given time is considerably less than with *iso*butyl alcohol.

The behaviour of 2-nitro-4 : 5-dimethoxybenzaldehyde, 3 : 6-dichloro-2-nitrobenzaldehyde, and 2 : 4 : 6-trinitrobenzaldehyde under similar treatment has been studied. The first named undergoes the same transformations as the parent substance. The dichloro-compound when dissolved in methyl or ethyl alcohol is converted under the influence of light into the corresponding acetal and 2 : 2′-azoxybenzoic acid derivatives, but esters of a dichloronitrosobenzoic acid are not formed, possibly because the intramolecular reaction

$$\begin{matrix}=CCl\\ -C(NO_2)\end{matrix}\!\!>C\cdot CH(OR)_2 \longrightarrow \begin{matrix}=CCl\\ -C(NO)\end{matrix}\!\!>C\cdot C(OR)_2\cdot OH$$

is prevented by steric hindrance; a solution of the aldehyde in benzene when acted on by sunlight yields 3 : 6-dichloro-2-nitrosobenzoic acid.

The formation of an ester of *o*-nitrosobenzoic acid by the decomposition of an *o*-nitrobenzaldehydeacetal undoubtedly takes place through the intermediate formation of the compound

$$NO\cdot C_6H_4\cdot C(OR)_2\cdot OH,$$

since under similar conditions *o*-nitrobenzaldehyde passes into *o*-nitrosobenzoic acid; consequently, it is extremely probable that the esterification of an acid proceeds through the mono-alkylated ortho-acid: $-CO_2H \xrightarrow{R\cdot OH} [-C(OH)_2\cdot OR] \longrightarrow -CO_2R + H_2O$, a suggestion first advanced by Henry.

The following acetals were prepared by the action of hydrogen chloride on a mixture of the aldehyde and alcohol; they were also obtained by exposing solutions of aldehyde in the necessary alcohol to the action of sunlight for a short time. *o-Nitrobenzaldehydediethylacetal*, $NO_2\cdot C_6H_4\cdot CH(OEt)_2$, is an aromatic, slightly yellow oil, b. p. 147·8—148·3°/11 mm., 154·8—155·3°/15 mm.; the corresponding *dipropylacetal*, $C_{13}H_{19}O_4N$, has b. p. 168°/10 mm.; the *di*iso*propylacetal* has b. p. 150°/12 mm.; the *di*iso*butylacetal* has b. p. 179°/11 mm.; 2-*nitro*-4 : 5-*dimethoxybenzaldehydedimethylacetal*,

$$C_{11}H_{15}O_6N,$$

crystallises in colourless, flat, glistening prisms, m. p. 54·5—55·5°.

Attempts to prepare the dimethylacetal of 2 : 4 : 6-trinitrobenzaldehyde were unsuccessful.

The following esters were prepared by acting on the requisite acetal with sunlight during a few hours; in the molten state they are green. *Propyl* o-*nitrosobenzoate*, $C_{10}H_{11}O_3N$, colourless, glistening prisms, m. p. 95°; iso*propyl* o-*nitrosobenzoate*, stout, white prisms, m. p. 117—118°; iso*butyl* o-*nitrosobenzoate*, $C_{11}H_{13}O_3N$, colourless,

compact needles, m. p. 99—99·5°; *methyl 2-nitroso-4 : 5-dimethoxybenzoate*, $C_{10}H_{11}O_5N$, faintly green, granular crystals, sinters at 125°, m. p. 126·5—127·5°.

3 : 6 : 3′ : 6′-Tetrachloro-2 : 2′-azoxybenzoic acid, $C_{14}H_6O_5N_2Cl_4$, is a pale yellow, crystalline powder, m. p. about 281—282° (decomp.), when heated in a bath from 265°. *3 : 6-Dichloro-2-nitrosobenzoic acid* forms small, faintly yellow crystals. *2-Nitro-4 : 5-dimethoxybenzaldoxime*, $C_9H_{10}O_5N_2$, crystallises in glistening, yellow needles, m. p. 178°, when heated in a bath from 168°. W. H. G.

Metallic Calcium and Absolute Alcohol as Reducing Agents. Charles Marschalk (*Ber.*, 1910, 43, 641—642).—Attempts have been made to reduce coumarone and benzophenone with metallic calcium and absolute alcohol. Coumarone is not affected, but benzophenone is reduced to benzhydrol. Sodium and alcohol, on the other hand, reduce coumarone to coumaran, and benzophenone to diphenylmethane (Klages and Allendorf, Abstr., 1898, i, 433). J. J. S.

Condensation of Cuminaldehyde with Methyl Propyl Ketone. Theodor St. Warunis and P. Lekos (*Ber.*, 1910, 43, 654—660. Compare Warunis, *Inaug. Diss.*, 1903).—Cuminaldehyde condenses with methyl propyl ketone, yielding two isomeric cuminylidenemethyl propyl ketones. These when reduced with sodium amalgam in acid solution yield isomeric cuminylmethyl propyl ketones. When treated with sodium hypochlorite according to Stoermer and Wehln's method (Abstr., 1903, i, 46), the unsaturated ketones yield cuminaldehyde.

α-Cuminylidenemethyl propyl ketone, $C_6H_4Pr^{\beta}\cdot CH{:}CH\cdot COPr^{\alpha}$, obtained by shaking the aldehyde and ketone with 10% sodium hydroxide solution, is a pale yellow liquid with b. p. 176—180°/14 mm. The *dibromide*, $C_{15}H_{20}OBr_2$, crystallises in plates, m. p. 124—125°. The *semicarbazone*, $C_{16}H_{23}ON_3$, has m. p. 163°. The *oxime*, $C_{15}H_{21}ON$, m. p. 122—123°, and the *phenylhydrazone*,

$$C_6H_4Pr^{\beta}\cdot CH{:}CH\cdot CPr^{\alpha}{:}N\cdot NHPh,$$

m. p. 111°. *α-Cuminylmethyl propyl ketone*,

$$C_6H_4Pr^{\beta}\cdot CH_2\cdot CH_2\cdot COPr^{\alpha},$$

is a colourless oil, with b. p. 155—160°/12 mm., and yields a *semicarbazone*, $C_{16}H_{25}ON_3$, m. p. 126°.

γ-Cuminylidenepropyl methyl ketone, $C_6H_4Pr^{\beta}\cdot CH{:}CEt\cdot COMe$, obtained by saturating a mixture of the aldehyde and ketone with hydrogen chloride, is a pale yellow oil, with b. p. 174—175°/15 mm. or 167°/12 mm. The *dibromide* is oily; the *semicarbazone*, $C_{16}H_{23}ON_3$, crystallises in needles, m. p. 198°, and the *oxime*, $C_{15}H_{21}ON$, in large crystals, m. p. 107°.

γ-Cuminylpropyl methyl ketone, $C_6H_4Pr^{\beta}\cdot CH_2\cdot CHEt\cdot COMe$, is a colourless liquid, b. p. 159—161°/14 mm.; its *semicarbazone*,

$$C_{16}H_{25}ON_3,$$

crystallises in plates, m. p. 135°.

The *semicarbazone* of cuminaldehyde, $C_6H_4Pr^{\beta}\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$, has m. p. 211°. J. J. S.

Compounds of Quinones with Esters of Amino-acids. Emil Fischer and Hans Schrader (*Ber.*, 1910, 43, 525—529).—By the addition of an alcoholic solution of benzoquinone to a cold alcoholic solution of ethyl glycine, quinol is formed, and also a red substance, $C_{14}H_{18}O_6N_2$, which from analogy to dianilinoquinone receives the constitution $C_6H_2O_2(NH\cdot CH_2\cdot CO_2Et)_2$, and the name *diethyl diglycinoquinone*. It separates from chloroform in red, quadratic plates, has m. p. 215° (corr.), develops a fine bluish-violet colour in cold alcoholic potassium hydroxide, and by treatment with bromine in chloroform yields *ethyl glycine hydrobromide*, m. p. 175—176° (decomp., corr.).

Diethyl dialaninoquinone, $C_6H_2O_2(NH\cdot CHMe\cdot CO_2Et)_2$, m. p. 140° (corr.), crystallising in red prisms, and *diethyl diglycinotoluquinone*, $C_6HMeO_2(NH\cdot CH_2\cdot CO_2Et)_2$, m. p. 162° (corr.), are similar substances obtained in a similar manner, the solvent in the former case being ether. C. S.

Oxidation of β-Naphthaquinone. C. H. Robinson (*J. Amer. Chem. Soc.*, 1910, 32, 117—119).—It has been found by Daly (Abstr., 1907, i, 407) that in the oxidation of β-naphthaquinone by an alkaline solution of potassium permanganate, the reaction ceases before the amount of permanganate has been reduced which is theoretically required to oxidise the naphthaquinone to phthalonic acid, and he has suggested that the acid $C_6H_4(CO\cdot CO_2H)_2$ may possibly be formed in the solution. Experiments have now been made which indicate that β-naphthaquinone is oxidised directly to phthalonic acid in alkaline solution without the formation of any intermediate compounds. E. G.

The Anthraquinone Series. Fritz Ullmann (*Ber.*, 1910, 43, 536—539).—In this preliminary paper the author summarises briefly the results of previous work on the mobility of halogen atoms in anthraquinone derivatives. His intention is to study anthraquinone derivatives in connexion with the problem of colour and constitution, and also to examine the affinity of their leuco-compounds for the fibre. C. S.

Preparation of Chloro- and Bromo-anthraquinonesulphonic Acids. Badische Anilin & Soda-Fabrik (D.R.-P. 216071).—The direct halogenation of anthraquinonesulphonic acids in aqueous solution does not proceed smoothly, owing to the frequent replacement of sulphonic groups by hydroxyl. It is found that if concentrated sulphuric acid, or that containing anhydride, is employed as solvent, and the required halogen introduced either in the presence or absence of a carrier, the reaction proceeds normally.

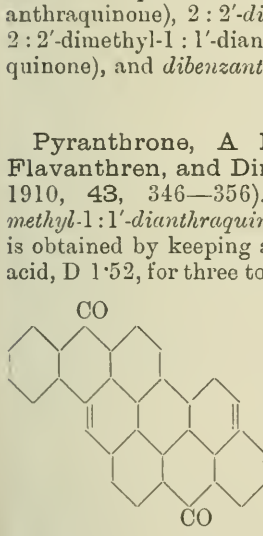
1 : 4-*Dichloroanthraquinone-β-sulphonic acid*, prepared by thus treating sodium anthraquinone-β-sulphonate with chlorine at 160° until the necessary increase of weight has been obtained, is a dark yellow powder, crystallising from 90% acetic acid in glistening, yellow scales. The position of the chlorine atoms was indicated by the formation of quinizarinsulphonic acid on replacement of halogen by hydroxyl.

Sodium bromoanthraquinonesulphonate, dark yellow, spear-shaped crystals, together with other more highly brominated acids, were prepared from sodium anthraquinone-β-sulphonate. F. M. G. M.

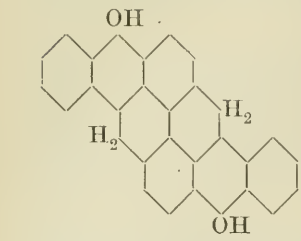
Preparation of Dianthraquinone Oxide. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 216268).—*$a\beta$-Dianthraquinone oxide* is prepared by condensing 1-chloroanthraquinone with 2-hydroxyanthraquinone in the presence of copper powder and fused sodium acetate in nitrobenzene solution; on cooling, the product separates in grey crystals, which are almost insoluble in all the ordinary solvents, except acetic acid. F. M. G. M.

Preparation of Dianthraquinonyl and of Dibenzanthronyl Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 215006).—Dianthraquinonyl derivatives have previously been prepared by treating the diazonium salts of aminoanthraquinones with copper in the presence of acetic anhydride (Abstr., 1907, i, 942); it is now found that the reaction will take place in dilute aqueous solutions containing copper salts, or such mixtures as cupric chloride and iron, ferric chloride and copper, potassium bromide and zinc dust, cupric chloride and hydroxylamine, or cupric chloride and sulphurous acid. The patent mentions 1 : 1′-*dianthraquinonyl* (from 1-aminoanthraquinone), 2 : 2′-*dianthraquinonyl* (from 2-aminoanthraquinone), 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (from 1-amino-2-methylanthraquinone), and *dibenzanthronyl*, prepared from aminobenzanthrone. F. M. G. M.

Pyranthrone, A Non-nitrogenous Methine Analogue of Flavanthren, and Dimethylpyranthrone. Roland Scholl (*Ber.*, 1910, 43, 346—356).—[With Christian Seer.]—*Dinitro*-2 : 2′-*dimethyl*-1 : 1′-*dianthraquinoyl*, $C_{30}H_{16}O_8N_2$, a yellow, crystalline substance, is obtained by keeping a solution of dimethyldianthraquinoyl in nitric acid, D 1·52, for three to five days at the ordinary temperature. By boiling for one to two hours with sodium hydroxide and sodium hyposulphite, it is reduced to the *diamino*-compound, $C_{30}H_{20}O_4N_2$, which forms dark red, microcrystalline octahedra. The conversion of dimethyldianthraquinoyl into *pyranthrone* (annexed formula) is effected by (1) heating at 350—380° for thirty minutes, (2) heating with zinc chloride at 280° for fifteen minutes, (3) heating with alcoholic potassium hydroxide for two hours at 140—145°. In the last method a blackish-red, hydrogenised compound is produced, which is converted into pyranthrone by passing air through the reaction mixture diluted with boiling water. Pyranthrone is a brown powder, which is insoluble in low boiling solvents, but separates from nitrobenzene in reddish-brown needles with a steel-blue lustre; it is carbonised by heating, gives a blue solution in concentrated sulphuric acid, is slowly oxidised by fusion with alkalis, and by reduction with alkaline hyposulphite yields a purplish-red vat,



which regenerates pyranthrone in the presence of air, and produces on unmordanted cotton lustrous, purplish-red colours, which change in air to orange-yellow or fiery-red shades of unrivalled fastness.



[With Julius Potschiwauscheg.]—The preceding vat probably contains the sodium derivative of tetrahydropyranthrone (annexed formula), because with ethereal *p*-bromobenzoyl chloride it yields *di*-p-*bromobenzoyltetrahydropyranthrone*, $C_{44}H_{24}O_4Br_2$, which forms yellow needles and does not melt below 360°. *Pyranthrene*, $C_{30}H_{18}$, is obtained by heating pyranthrone, red phosphorus, and hydriodic acid, D 1·7, for seven hours at 165—175°. It has m. p. above 360°, crystallises in brown needles or yellowish-green prisms, develops a violet-blue coloration in sulphuric acid, and forms a fluorescent solution in xylene and a non-fluorescent solution in nitrobenzene.

4-*Nitro*-1 : 3-*dimethylanthraquinone*, m. p. 234°, is obtained by boiling dimethylanthraquinone with nitric acid, D 1·37, for ten hours; it is reduced by sodium hydroxide and sodium hyposulphite to the *amino*-compound, m. p. 235—236°. 2 : 4-*Dinitro*-1 : 3-*dimethylanthraquinone*, m. p. 283—285°, is obtained by agitating dimethylanthraquinone with nitric acid, D 1·52, for ten hours at the ordinary temperature; the *diamino*-compound has m. p. 230° (decomp.). 4-*Iodo*-1 : 3-*dimethylanthraquinone*, $C_{16}H_{11}O_2I$, m. p. 118—119°, obtained from diazotised 4-amino-1 : 3-dimethylanthraquinone and potassium iodide, is converted by Ullmann's copper process at 210—250° into 2 : 4 : 2′ : 4′ *tetramethyl*-1 : 1′-*dianthraquinoyl*, $C_6H_4<^{CO}_{CO}>C_6HMe_2\cdot C_6HMe_2<^{CO}_{CO}>C_6H_4$, m. p. 296—298°, which by treatment with alcoholic potassium hydroxide at 135°, and subsequent oxidation of the product by air, yields 4 : 4′-*dimethylpyranthrone*, $C_{32}H_{18}O_2$. The latter separates from nitrobenzene in orange-red needles, and yields with alkaline hyposulphite a purplish-red vat, which develops on unmordanted cotton purplish-red shades changing to a fine golden-yellow in air. 4 : 4′-*Dimethylpyranthrene*, $C_{32}H_{22}$, crystallises in brown needles, and forms a fluorescent solution in *m*-xylene. C. S.

Monoterpenes, Limonenes, and Carvones. Ernst Deussen and Alfred Hahn (*Ber.*, 1910, **43**, 519—524).—The new *d*-β-carvoxime (Abstr., 1909, i, 502) can be obtained from either *d*-α- or β-limonenenitrosochloride by elimination of hydrogen chloride. In a similar way, *l*-limonenenitrosochloride yields, in addition to *d*-carvoxime, an oil, which forms a *benzoyl* derivative, m. p. 76—77°, $[\alpha]_D$ − 73·58° in benzene, from which *l*-β-*carvoxime*, m. p. 56—57°, is obtained by hydrolysis by alcoholic potassium hydroxide.

d-Limonene-α-nitrolanilide and also *d*-limonene-β-nitrolanilide, when heated at 140°/12 mm., yield aniline and *l*-α-carvoxime. *l*-α-Carvoxime is converted into *i*-carvoxime by prolonged heating in alcohol or petroleum, and *l*-hydrochlorocarvoxime is also rendered inactive by

heating its methyl-alcoholic solution; the benzoyl and the phthalyl esters of *l*-α-carvoxime, however, remain unaltered under these conditions. *l*- and *d*-α-Benzoylcarvoximes yield by bromination *tetrabromo*-compounds, each having m. p. 135—136°; that derived from *l*-α-benzoylcarvoxime has $[\alpha]_D$ +25·97°, and that from the *d*-isomeride, −[25·51°], in benzene. C. S.

Ethereal Oils Free from Terpenes and Sesquiterpenes. Erich Böcker (*J. pr. Chem.*, 1910, [ii], **81**, 266—281).—Frequently the odour of a natural ethereal oil is prejudicially affected, and its solubility in alcohol largely diminished, by the presence of terpenes and sesquiterpenes. A table is given comparing the specific gravity, rotation, solubility in alcohol of different strengths, saponification, ester, acid and acetylation numbers, aldehyde and phenol content, and the solidifying point of sixty-three natural ethereal oils with those of the oils left after the removal of the hydrocarbons by processes which are trade secrets. C. S.

Occurrence of Camphene in Rosin Spirit. Carlo Grimaldi (*Chem. Zeit.*, 1910, **34**, 220).—In an earlier communication (Abstr., 1909, i, 943) the author recorded the occurrence of camphene in "spirits" prepared from American and Austrian colophony, but only in small quantities. He has now succeeded in isolating it in the pure state. E. J. R.

Characters, Distinction, and Detection in Plants of Arbutin and Methylarbutin. Émile Bourquelot and Mlle. A. Fichtenholz (*J. Pharm. Chim.*, 1910, [vii], **1**, 62—66, 104—109).—The arbutin of commerce is now known to be a mixture of true arbutin with methylarbutin (compare Bourquelot and Hérissey, Abstr., 1908, i, 356), and in the present paper the constants and reactions of the two substances are detailed with a view to facilitating their identification in plants. Arbutin is hydrolysed by emulsin, yielding quinol and dextrose, and the cupric-reducing power of the solution resulting from the action of emulsin on a solution of the glucoside is due to both these substances. Owing to the presence in emulsin of a small amount of an oxydase, the quinol formed by the hydrolysis of arbutin in this way becomes slightly oxidised, and the solution assumes a yellowish-brown colour. This oxidation does not seriously affect the cupric-reducing power of the product so long as the action is not allowed to go on for more than eight days. Arbutin gives a blue coloration with ferric chloride solution, and a sapphire-blue colour with Jungmann's reagent.

Methylarbutin on hydrolysis by emulsin furnishes quinol methyl ether and dextrose, and the cupric-reducing power of the hydrolysed product and its rotation are due to the latter only. On hydrolysis with emulsin, a solution of methylarbutin does not darken in colour even if an oxydase is added. Further, it is hydrolysed much more rapidly than arbutin (compare Abstr., 1908, ii, 995; 1909, i, 862), and gives no coloration with either ferric chloride solution or Jungmann's reagent, although quinol methyl ether gives, like arbutin, a blue colour with each of these reagents.

For the detection of either of these glucosides in presence of the other, determination of the rotation before and after hydrolysis with emulsin is recommended, the colour reactions mentioned being used for confirmatory evidence. T. A. H.

Glucosidic Acids of Convolvulin and the Composition of Crude *iso*Rhodeose. Emil Votoček (*Ber.*, 1910, 43, 476—482).—Convolvulin is resolved by hydrolysis with alkali into α-methylbutyric acid and two glucosidic acids, the crystalline convolvulinic acid and amorphous purgic acid. Convolvulinic acid, when hydrolysed with acids, forms convolvulinolic acid, dextrose, rhodeose, and a sugar which gives rise to mucic acid when its hydrogen cyanide additive product is oxidised; this is now proved to be rhamnose. Purgic acid is converted by acid hydrolysis into decenoic acid, hydroxylauric acid, and syrupy *iso*rhodeose; the last contains only methylpentoses, and has $[\alpha]_D$ + 25°; it forms no mucic acid when the hydrogen cyanide additive product is oxidised. The *phenylosazone* has m. p. 183—184°, the p-*bromophenylosazone* has m. p. 217°, whilst *rhodeose*-p-*bromophenyl hydrazone* has m. p. 202—204°. Crystalline hydrazones could not be obtained. E. F. A.

Aloin. Otto A. Oesterle and G. Riat (*Schweiz. Woch. Chem. Pharm.*, 1909, 717—721. Compare Oesterle, Abstr., 1899, i, 538; 1900, i, 304; Tschirch and Pedersen, Abstr., 1898, i, 599; Jowett and Potter, Trans., 1905, 87, 878; Robinson and Simonsen, *ibid.*, 1909, 95, 1085).—Aloe-emoidin and a sugar are formed when aloin is boiled for some eighty hours with sulphuric acid and 95% alcohol, or for twenty-four to thirty-six hours with alcohol and hydrochloric acid. The sugar gave an osazone, m. p. 208—209°.

The oxidation of aloin with sodium peroxide (Léger, Abstr., 1902, i, 549) has been studied. The best yields are obtained when 30 grams of aloin are warmed with 500 c.c. of water at 70—80°. Thirty grams of the peroxide are added gradually and with constant stirring. The addition of hydrochloric acid precipitates crude aloe-emoidin (compare Jowett and Potter). J. J. S.

Tetrahydrothiophen and *cyclo*Pentamethylene Sulphide. Julius von Braun and A. Trümpler (*Ber.*, 1910, 43, 545—551).—Whilst substances containing four-, five-, six-, seven-, sixteen-, and eighteen-membered rings of carbon and at least two atoms of sulphur are formed easily and sometimes quantitatively from acyclic generators, the production of heterocyclic systems containing only one atom of sulphur is accompanied by anomalies, the comparatively easy formation of thiophen being in strong contrast to the difficulty of obtaining methylpenthiophen (Krekeler, Abstr., 1887, 239). The authors have prepared compounds of the type $(CH_2)_x{>}S$, and encounter similar anomalies. *Tetrahydrothiophen*, $\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}{>}S$, b. p. 119°, is obtained in almost quantitative yield when an alcoholic solution of αδ-di-iodobutane is added to a concentrated aqueous

solution of potassium sulphide, whilst under similar conditions the yield of *pentamethylene sulphide* [*pentahydropenthiophen*],

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>S,$$

b. p. 141°, from αε-di-iodopentane is less than 30%. Tetrahydrothiophen and pentamethylene sulphide, which form *methiodides* volatilising at 185—190° and 192° respectively, are very reactive substances, but their thorough examination has been postponed for the present on account of their insufferable odour. C. S.

Action of Cyanogen Bromide on Brucine and Strychnine. Gustav Mossler (*Monatsh.*, 1910, 31, 1—22).—Since brucine and strychnine probably contain a tetrahydroquinoline or a dihydroindole skeleton in which the nitrogen atom is linked to a nuclear carbonyl group, the author has applied to the two alkaloids Braun's methods of rupturing heterocyclic nitrogenous systems by means of phosphorus pentachloride (Abstr., 1904, i, 918) or cyanogen bromide (Abstr., 1900, i, 430). The attack of the former reagent does not lead to definite results, but by the action of cyanogen bromide in chloroform, additive compounds are formed which cannot be isolated in a pure state. The compound obtained from strychnine is decomposed by water, yielding ammonia and the hydrobromide of the alkaloid. The additive compound of cyanogen bromide and brucine is further attacked by the reagent in two directions, according to the experimental conditions. When cyanogen bromide is added slowly to a cold solution of brucine in chloroform, crystals are obtained of a *substance*,

$$C_{47}H_{52}O_8N_5Br,CHCl_3,3H_2O,$$

which by heating at 110° and crystallisation from 70% alcohol yields crystals of the composition $C_{47}H_{52}O_8N_5Br,2H_2O$; both have m. p. 203—205° (decomp.). The substance, which does not possess basic properties and retains its halogen in the presence of cold alkali, is regarded as a quaternary ammonium bromide produced by the rupture of one brucine molecule by the cyanogen bromide and the combination of the resulting brominated cyanamide with a second molecule of brucine.

When a solution of brucine in chloroform is added to an excess of cyanogen bromide in the same solvent, and the mixture is treated with 90% alcohol, a precipitate is obtained which by solution in water and reprecipitation by alcohol yields needles of a *hydrobromide*,

$$C_{23}H_{26}O_4N_2,HBr,4H_2O,$$

containing two methoxyl groups and decomposing at 250°. The free base, allo*brucine*, $C_{23}H_{26}O_4N_2,5H_2O$, is isomeric with brucine, into which it is converted by crystallisation from boiling water, but differs from it in containing water of crystallisation, in its rotation, $[\alpha]_D^{18}$ – 112·6°, in chloroform, m. p., and derivatives. The hydrated base melts at 69·5°, resolidifies at 75—80°, softens at 120—130°, and fuses again at about 182° (decomp.). The anhydrous base melts at 126—128° to a transparent, indistinctly liquid substance, becomes opaque, and then melts at about 182° (decomp.) *allo*Brucine, which is a monoacidic base, exhibits all the colour reactions of brucine. The *hydrochloride*, $C_{23}H_{26}O_4N_2,HCl,4H_4O$, crystallises in leaflets which effloresce

in air; the *methiodide*, $C_{23}H_{26}O_4N_2$,MeI,$1\frac{1}{2}H_2O$, has m. p. 265° (decomp.). When *allo*brucine is warmed with hydrogen peroxide, a *peroxide*, $C_{23}H_{26}O_6N_2$, is obtained, which contains $5H_2O$ when dried in air and H_2O when dried in a vacuum, and at 110° is converted into the *oxide*, $C_{23}H_{26}O_5N_2,H_2O$, which is also produced by heating an aqueous solution of the peroxide with platinum-black. The two hydrated peroxides and the oxide all have m. p. 182° (decomp.); by very rapid heating, the air-dried peroxide decomposes at 115—120° and the monohydrate at 150—152°, both resolidifying and then melting again at 182°. An aqueous solution of the peroxide is neutral and optically inactive, liberates iodine from potassium iodide, bleaches litmus, and exhibits the reactions of hydrogen peroxide when treated with potassium dichromate and sulphuric acid.

allo*Brucic acid*, $C_{23}H_{28}O_5N_2,7H_2O$, obtained by the action of sodium ethoxide on *allo*brucine, crystallises in yellow needles, has m. p. 165—166° (decomp.) when anhydrous, forms a nitrosoamine, the *hydrochloride* of which, $C_{23}H_{28}O_6N_3Cl$, carbonises at 210°, and is stable in boiling water, but is converted by cold acids into the corresponding brucine salts. C. S.

Hofmann's Iodomethylation of Cinchotoxine. I. Constitution of Freund and Rosenstein's Dimethylcinchonine. Ezio Comanducci (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 240—254).—Assuming the accuracy of the formula

$$C_9NH_6\cdot CO\cdot CH_2\cdot CH_2\cdot CH\begin{matrix}<\text{CH(CH:CH}_2\text{)}\\ \text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\end{matrix}>CH_2$$

for α-cinchonicine (cinchotoxine) (compare Abstr., 1909, i, 409), the dimethylcinchonine prepared by Freund and Rosenstein (Abstr., 1894, i, 151) will have one of the two formulæ:

$C_9NH_6\cdot CO\cdot CH_2\cdot CH_2\cdot CH(CH_2\cdot CH_2\cdot NMe_2)\cdot C(CH{:}CH_2){:}CH_2$ (I)

and $C_9NH_6\cdot CO\cdot CH_2\cdot CH_2\cdot CH(CH{:}CH_2)\cdot CH(CH{:}CH_2)\cdot CH_2\cdot NMe_2$ (II).

The author's experiments show that oxidation of dimethylcinchonine (1 mol.) by means of cold permanganate yields 1 mol. of formic acid, together with an unsaturated acid compound, which is named dimethylcinchotenine, thus: $-CH{:}CH_2 + 4O \longrightarrow H\cdot CO_2H + -CO_2H$.

[With Onofrio D'Onghia.]—*Dimethylcinchoninephenylhydrazone*, $C_{19}H_{20}N_2Me_2{:}N_2HPh$, forms yellow, mamillary crystals, m. p. 101—103°.

Tetrabromodimethylcinchonine hydrobromide,

$$C_{19}H_{16}ON_2Br_4Me_2,2HBr,$$

forms a dark yellow, deliquescent powder, m. p. 20—22°. The *picrate*, $C_{19}H_{16}ON_2Br_4Me_2,HBr,C_6H_3O_7N_3$, forms a lemon-yellow, crystalline powder, m. p. 143—145°. The *platinichloride*,

$$C_{19}H_{16}ON_2Br_4Me_2,H_2PtCl_6,$$

is obtained as a dark yellow powder, m. p. 230°, and the *aurichloride*, $C_{19}H_{16}ON_2Br_4Me_2,2HAuCl_4$, in reddish-yellow granules, m. p. 85° (decomp.).

Dimethylcinchotenine forms a reddish-brown powder with an acid reaction, and turns brown and contracts at 250°. Its *dibromo*-derivative, $C_{18}H_{16}ON_2Br_2Me_2\cdot CO_2H$, is obtained as a reddish-brown powder, which contracts at 200°, but does not melt at 250°. T. H. P.

Synthesis of Pyrrole Derivatives: Pyrroles from Ethyl Succinylosuccinate and from Azines. Oscar Piloty (*Ber.*, 1910, 43, 489—498).—Piloty and Quitmann (this vol., i, 133) have shown that hæmopyrrole and hæmopyrrolecarboxylic acid are trisubstituted pyrrole derivatives, and consider that the hæmatin or hæmin molecule, $C_{34}H_{34}O_4N_4FeCl$ or $C_{34}H_{32}O_4N_4FeCl$, contains each of these units repeated twice. Four such units contain 52 atoms of hydrogen, so that 20 or 18 atoms must be eliminated in the condensation.

One method of realising this is the formation of an intermediate ring from the side-chains of two molecules. Tryptophan, for example, might condense to yield derivatives of the parent substance,

$$CH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CH{-}C\cdot CH_2\cdot C\cdot NH\\ \|\quad\quad\quad\quad\|\\ NH\cdot C\cdot CH_2\cdot C{-}CH\end{matrix}\begin{matrix}\diagdown\\\diagup\end{matrix}CH,$$

which may be termed *hydropyrrindole*. The possibility of tryptophan having some relation to the colouring matter of blood has already been emphasised by Abderhalden.

Knorr's pyrrole synthesis can be extended to the condensation of 2 mols. of aminoacetone with 1 mol. of ethyl succinylosuccinate, forming *dimethylhydropyrrindole*, $CH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CMe\cdot C\cdot CH_2\cdot C{-}NH\\ \|\quad\quad\quad\quad\|\\ NH{-}C\cdot CH_2\cdot C\cdot CMe\end{matrix}\begin{matrix}\diagdown\\\diagup\end{matrix}CH.$

This substance is inclined to polymerise, and forms red, green, and violet dyes when oxidised. The full investigation has been delayed by the poor yields obtained, the constitution being assumed from the method of formation.

A more promising method of obtaining pyrrole derivatives is by the action of zinc chloride at high temperatures on the azines of aliphatic ketones. Bisdiethylazinemethylene gives rise to 3 : 4-*dimethyl*-2 : 5-*diethylpyrrole*, $NH\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}CEt{:}CMe\\ |\quad\quad|\\ CEt{:}CMe\end{matrix}$.

The condensation of aminoacetone hydrochloride with ethyl succinylosuccinate takes place in sodium hydroxide solution. *Dimethylhydropyrrindole*, purified by sublimation in a vacuum, forms colourless, lustrous, nacreous plates, which sinter at 260°, m. p. 271°. It gives a cherry or violet-red coloration with ferric chloride.

By the action of solid potassium hydroxide on aminobutanone hydrochloride, tetramethylpyrazine is formed, m. p. 86—87°, together with a pyrrole derivative, which was not obtained crystalline and decomposed into tetramethylpyrazine when distilled.

3 : 4-*Dimethyl*-2 : 5-*diethylpyrrole* is obtained as a faintly yellow-coloured oil, b. p. 133—135°/55 mm. The ethereal solution becomes dark brown on the addition of picric acid without yielding a picrate. It forms an amorphous *potassium* salt. The *acetate* is a light yellow oil, b. p. 180—184°/88 mm. E. F. A.

Anthranil. XVII. Heller's Recent Experiments in Connexion with Anthranil. Eugen Bamberger (*J. pr. Chem.*, 1910, [ii], 81, 254—265).—To disprove Heller's statement that aniline, not anthranil, is the product obtained by heating anthroxanic acid with water at 150° (Abstr., 1909, i, 832), the author has performed nine experiments in which anthroxanic acid (1 gram) is heated with 40—60 grams of water

at temperatures between 145° and 156° and for periods varying between three and four hours, and in every case anthranil can be detected by its odour, and frequently, also, by the formation of the mercurichloride.

In reply to Heller's contention (*loc. cit.*) that 23% hydrochloric acid and sodium nitrite act as a chlorine generator, the author shows that the nitrite produces less than 0·5% of chlorine from hydrochloric acid of this dilution. C. S.

[Preparation of Isatin Derivatives.] Kalle & Co. (D.R.-P. 215785. Compare Abstr., 1907, i, 1073).—Alkyloxyisatins having the general formula $OR\cdot C_6H_4\langle{}^{CO-}_{NH}\rangle CO$, R = alkyl, can be readily obtained by known methods for the preparation of isatins.

7-Methoxyisatin, $OMe\cdot C_6H_3\langle{}^{CO-}_{NH}\rangle CO$, bluish-red needles, m. p. 240—242°, is formed (1) by the oxidation of dimethoxyindigotin, (2) from the cyanohydrin of di-*o*-methoxycarboxydiphenylimide, (3) from di-*o*-anisyloxalimide chloride (Abstr., 1908, i, 695). *5-Methoxyisatin*, prepared from *o*-nitro-*m*-methoxybenzaldehyde, forms brownish-red needles, m. p. 200—202°.

The condensation products from these compounds with 3-oxy-(1)-thionaphthen and with 6-ethoxy-3-oxythionaphthen-2-carboxylic acid form valuable vat dyes. F. M. G. M.

Indigoid Dyes. VI. A. Felix and Paul Friedländer (*Monatsh.*, 1910, 31, 55—79. Compare Abstr., 1908, 673, 674; 1909, 415, 417; this vol., i, 176).—Indigoid dyes are obtained by the action of α-isatin chloride or anilide on keto- and diketo-hydrindene, various coumaranones, and dihydroxy*iso*quinolines. The dyes are very similar to indigotin, but give redder shades, and are more sensitive towards alkalis; they are sparingly soluble, crystalline substances, which can be sublimed and be reduced in alkaline solution to easily oxidisable leuco-compounds. The following dyes of these types have been prepared: 2-*Indane*-2-*indole-indigo* [2(2′)-*indoxyl*-3-*indanone*],

$$C_6H_4\langle{}^{CO-}_{CH_2}\rangle C{:}C\langle{}^{CO-}_{NH}\rangle C_6H_4,$$

prepared by heating equal molecular quantities of hydrindone and isatin chloride in benzene, crystallises in red needles, and is reduced by alkaline hyposulphite to a yellow vat, from which cotton is dyed bluish-red. 2(2′)-*Indoxyl*-1 : 3-*indandione*,

$$C_6H_4\langle{}^{CO-}_{CO-}\rangle C{:}C\langle{}^{CO-}_{NH}\rangle C_6H_4,$$

obtained in a similar manner from diketohydrindene, forms brownish-violet needles, and is decomposed by warming with 5% sodium hydroxide, yielding anthranilic acid and 3-*hydroxy*-1-*indenone*-2-*aldehyde*, $C_6H_4\langle{}^{C(OH)}_{-CO-}\rangle C\cdot CHO$, m. p. 139·5°, which separates from hot water in white, and from organic solvents in red needles, reacts with hydrazine and phenylhydrazine, develops a cherry-red colour with ferric chloride, and forms yellow alkali salts which are not decomposed by acetic acid. 5 : 6-*Dimethoxy*-1(2′)-*indoxylcoumaranone*

$C_6H_2(OMe)_2<^{CO}_{O}>C{:}C<^{CO}_{NH}>C_6H_4$, obtained from *a*-isatinanilide and dimethoxycoumaranone in naphtha, forms copper-red crystals, which yield a reddish-violet vapour almost without decomposition. Hydroxymethoxycoumaranone and isatinanilide under similar conditions yield an analogous indigoid dye, $C_{17}H_{11}O_5N$. Both of these dyes in alcoholic or acetic acid solution react with aldehydes in the presence of sodium carbonate or hydrochloric acid to form oxygen isologues of the indogenides, of which the following are described:

$C_6H_2(OMe)_2<^{CO}_{O}>C{:}CHPh$, from benzaldehyde, yellow prisms, m. p. 148—149°.

$C_6H_2(OMe)_2<^{CO}_{O}>C{:}CH\cdot C_6H_4\cdot OH$, from salicylaldehyde, orange-yellow needles, m. p. above 240°.

$C_6H_2(OMe)_2<^{CO}_{O}>C{:}CH\cdot C_6H_4\cdot OH$, from *m*-hydroxybenzaldehyde, yellow needles, m. p. 202·5—203°.

$C_6H_2(OMe)_2<^{CO}_{O}>C{:}CH\cdot C_6H_4\cdot OH$, from *p*-hydroxybenzaldehyde, citron-yellow crystals.

$C_6H_2(OMe)_2<^{CO}_{O}>C{:}CH\cdot C_6H_2(OH)_2$, from protocatechualdehyde, orange-yellow needles, m. p. 217°.

The *dimethoxycoumaranone*, m. p. 122·5—123°, required in the preceding preparation is obtained by adding an excess of methyl sulphate to a warm solution of ω-chlorotrihydroxyacetophenone (obtained from pyrogallol and chloroacetic acid) in aqueous sodium carbonate. In faintly alkaline solution, and with a deficit of methyl sulphate, the monomethylated *derivative*, m. p. 197°, is also produced. A dilute alcoholic solution of equal molecular quantities of dimethoxycoumaranone and β-naphthaquinone-4-sulphonic acid, by treatment with aqueous sodium carbonate, yields the sodium salt of 5′ : 6′-*dimethoxycoumaranonyl*-1-*hydroxy*-4-*oxynaphthalene*,

$$C_6H_2(OMe)_2<^{CO}_{O}>C{:}C<^{\text{---}C_6H_4\text{---}}_{CH{:}C(OH)}>CO,$$

which crystallises in orange-brown needles. 3(2′)-*Indoxyl*-3-iso*quinoline*-1 : 4-*dione*, $C_6H_4<^{CO\cdot C}_{CO\cdot NH}>C<^{CO}_{NH}>C_6H_4$, prepared from *a*-isatin chloride or anilide and dihydroxy*iso*quinoline, forms dark blue needles, and is reduced by alkaline hyposulphite to an orange-red vat, from which the dye is regenerated in the air.

Indigoid dyes have also been produced by the action of isatin chloride or anilide on rhodanic acid, methylpyrazolone, phenylmethylpyrazolone, and barbituric acid. The increased aliphatic character of these dyes is accompanied by increased sensitiveness towards acids and, especially, alkalis. 5-*Keto*-4(2′)-*indoxyl*-1-*phenyl*-3-*methylpyrazole*, $^{NPh\cdot CO}_{N=CMe}>C{:}C<^{CO}_{NH}>C_6H_4$, obtained from phenylmethylpyrazolone and isatin-*a*-anilide in boiling xylene, separates

from nitrobenzene in almost black plates, gives a light yellow vat with alkaline hyposulphite, and is decomposed by boiling 10% sodium hydroxide, yielding anthranilic acid and 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*aldehyde*, $COH\cdot C\begin{matrix}C(OH)\cdot NPh\\ CMe{=}N\end{matrix}$, m. p. 173—174°. This aldehyde is amphoteric, the acid character predominating; it forms a fairly stable *silver* salt, a *phenylhydrazone*, m. p. 159°, an *aldazine*, m. p. 290°, and the *azomethine* derivative, $\begin{matrix}NPh\cdot C(OH)\\ N{=}{=}CMe\end{matrix}\!\!>C\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, m. p. 240°, with anthranilic acid in the presence of dilute acids. 4(2′)-*Indoxyl*-3-*methyl*-4-*pyrazole*, $\begin{matrix}NH\cdot CO\\ N{:}CMe\end{matrix}\!\!>C{:}C<\begin{matrix}CO\\ NH\end{matrix}\!\!>C_6H_4$, obtained from equal molecular quantities of 3-methylpyrazolone and isatinanilide in nitrobenzene at 150°, separates from alcohol or dilute acetic acid in dark violet needles; it possesses pronounced basic properties, and is easily decomposed by alkali hydroxides. 4-*Keto*-2-*thio*-5(2′)-*indoxyl*-*thiazole*, $\begin{matrix}NH\cdot CO\\ CS{-}{-}S\end{matrix}\!\!>C{:}C<\begin{matrix}CO\\ NH\end{matrix}\!\!>C_6H_4$ or $\begin{matrix}N{-}{-}CO\\ C(SH)\cdot S\end{matrix}\!\!>C{:}C<\begin{matrix}CO\\ NH\end{matrix}\!\!>C_6H_4$, obtained by heating rhodanic acid and α-isatinanilide in acetic anhydride, forms almost black needles. 4-*Keto*-2-*thio*-5(2′)-*thionaphthenyl*-*thiazole*, $\begin{matrix}NH\cdot CO\\ CS{-}{-}S\end{matrix}\!\!>C{:}C<\begin{matrix}CO\\ S\end{matrix}\!\!>C_6H_4$, obtained from thioisatinanilide and rhodanic acid in a similar manner, forms reddish-brown needles. 5(2′)-*Indoxylpyrimidine*-2 : 4 : 6-*trione*,

$$CO<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}\!\!>C{:}C<\begin{matrix}CO\\ NH\end{matrix}\!\!>C_6H_4,$$

prepared from barbituric acid and α-isatinanilide in acetic anhydride, forms orange-red needles.

The absorption spectra of those indigoid dyes which differ from indigotin by containing, in the place of one of the NH groups, the atoms or groups: S, CH:CH, CO·NH, CH_2, or CO, are plotted, and the influence of these replacements on the colour are briefly discussed.

C. S.

Coloured Salts of Schiff's Bases. III. Salts of Bases Formed by Condensing *m*-Aminodimethylaniline and *m*-Aminodiethylaniline with Aromatic Aldehydes. Forris J. Moore (*J. Amer. Chem. Soc.*, 1910, **32**, 382—388).—It has been shown in earlier papers (Moore, Abstr., 1908, i, 368; Moore and Woodbridge, Abstr., 1908, i, 686) that benzylidene compounds of the type $R\cdot CH{:}N\cdot C_6H_4\cdot NR'R''$ unite with hydrogen chloride in two proportions, forming dark red hydrochlorides and yellow dihydrochlorides.

The present work was undertaken with the object of determining whether the difference in the colour of these salts is due to the dark-coloured salts having a quinonoid constitution. In order to test this, it was decided to prepare analogous compounds of such a structure that they could not readily assume the quinonoid form, and to study their salts. It seems probable that the bases previously used in this work would readily form quinonoid salts, since, in all cases, the two

nitrogen atoms were in the para-position to each other. This behaviour, however, would not be expected from the analogous meta-compounds.

as-Dimethyl-*m*-phenylenediamine and *as*-diethyl-*m*-phenylenediamine condense readily with benzaldehyde, anisaldehyde, cinnamaldehyde, and piperonaldehyde to form *compounds*, which on treatment with hydrogen chloride invariably yield light-coloured *salts*. This behaviour seems at first sight to indicate that the dark-coloured salts of the corresponding *p*-compounds have a quinonoid structure, but this inference is weakened by the fact that the *m*-bases are polymerides, and can only be obtained in an amorphous condition.

m-Nitrodiethylaniline and *as*-diethyl-*m*-phenylenediamine *picrates* melt at 138° and 152° respectively. E. G.

Preparation of Benzophenoneimine Derivatives. Forris J. Moore (*Ber.*, 1910, 43, 563—565. Compare Reddelien, this vol., i, 118).—Diphenylmethylenedimethyl-*p*-phenylenediamine, m. p. 86°, is readily obtained by heating together equivalent quantities of benzophenone and *p*-aminodimethylaniline with finely-powdered barium oxide in an atmosphere of hydrogen at 180°. With other amines the condensation proceeds more readily in the absence of the barium oxide. Thus benzophenonephenylimine is readily obtained by heating benzophenone and aniline for an hour at 210°.

Benzophenoneimine hydrobromide is readily obtained by passing ammonia into a chloroform solution of diphenyldibromomethane (Friedel and Balsohn, Abstr., 1880, 558). It crystallises in colourless needles and reacts with water, yielding benzophenone. The free base can be obtained by Hantzsch's (Abstr., 1892, 338) or Thomae's (Abstr., 1905, i, 718) method.

A small amount of the hydrobromide is also formed by the action of magnesium phenyl bromide on benzobromoamide. J. J. S.

Preparation of Dianthraquinonylphenylenediamine. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 215294).—*Dianthraquinonylphenylenediamine*, $C_6H_4(NH\cdot C_6H_3<^{CO}_{CO}>C_6H_4)_2$, is prepared by condensing aminoanthraquinone with *p*-dichlorobenzene in the presence of naphthalene, sodium acetate, and cupric chloride at 200—215°. The product crystallises from nitrobenzene in black needles; the solution in concentrated sulphuric acid is greenish-yellow, from which water precipitates a violet-red powder. F. M. G. M.

Tetramethyldiaminobenzophenone and Dianilinodiphenylmethane. Fritz Straus and Richard Bormann (*Ber.*, 1910, 43, 728—739).—The authors cannot state with certainty that the blue compounds obtained by the action of carbonyl chloride on tetramethyldiaminobenzophenone (Staudinger, Abstr., 1909, i, 905) and tetramethyldiaminothiobenzophenone (Baither, Abstr., 1887, 816) are identical; the bishydrochloride of the former is colourless, that of the latter yellow, becoming colourless in the presence of excess of hydrogen chloride and yellow again when kept over potassium hydroxide.

Di-p-*nitro*-o-*sulphoanilinodiphenylmethane*, $CH_2[C_6H_4\cdot NH\cdot C_6H_3(NO_2)\cdot SO_3H]_2$, obtained in the form of the sodium salt by heating diaminodiphenylmethane with an aqueous solution of sodium hydrogen carbonate and sodium *p*-nitrochlorobenzene-*o*-sulphonate (3 mols.), is an orange-yellow powder. If only 2 mols. of the sulphonate are used, the chief product is the sodium salt of *amino*-p-*nitro*-o-*sulphoanilinodiphenylmethane*, $NH_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)\cdot SO_3H$, a citron-yellow powder. An aqueous solution of the sodium salt of the disulphonate is reduced by zinc dust and ammonium chloride to the corresponding *amino*-compound, $C_{25}H_{24}O_6N_4S_2$, which is converted by concentrated hydrochloric acid at 100° into the *hydrochloride*, $C_{25}H_{24}N_4,4HCl$, of di-*p*-aminophenyldiaminodiphenylmethane. The *base* itself, m. p. 131°, forms white needles; its alcoholic solution, when treated in a freezing mixture with concentrated sulphuric acid and amyl nitrite, and subsequently with copper powder, yields p : p-*dianilinodiphenylmethane*, $CH_2(C_6H_4\cdot NHPh)_2$, m. p. 114°, which is soluble in concentrated acids.

C. S.

Magnesium Alkyl Haloids and Aldazines. Max Busch and Martin Fleischmann (*Ber.*, 1910, **43**, 740—750).—Franzen and Deibel found that benzaldazine was reduced to benzaldehydebenzylhydrazone by magnesium ethyl bromide (Abstr., 1905, i, 843). The authors find that, in addition to this reaction, which may proceed to the extent of forming dibenzylhydrazine, the normal addition occurs, the course of the reaction being most conveniently followed by the use of magnesium aryl halides. Thus the product of the interaction of benzaldazine and magnesium phenyl bromide in ether, when decomposed by dilute hydrochloric acid at 0°, yields a mixture of the hydrochlorides of benzaldehydebenzylhydrazone and benzaldehydediphenylmethylhydrazone. The *hydrazone* itself, $CHPh_2\cdot NH\cdot N{:}CHPh$, decomposes at 85°, explodes very readily, and easily loses its nitrogen, yielding products from which tetraphenylethane and diphenylmethane have been isolated. To account for their formation, the authors offer the suggestion that the hydrazone changes into the azo-compound, $CHPh_2\cdot N{:}N\cdot CH_2Ph$, which then decomposes like Thiele's azomethane, yielding nitrogen, diphenylmethyl, and benzyl, from the last two of which the two hydrocarbons in question are generated. The interaction of magnesium benzyl chloride and benzaldazine, and the treatment of the product successively with ice-water, acetic acid, ammonium chloride, and excess of ammonium hydroxide, lead to the formation of *benzaldehydediphenylethylhydrazone*, $CHPh{:}N\cdot NH\cdot CHPh\cdot CH_2Ph$, m. p. 104—105° (decomp.), which forms a *hydrochloride*, m. p. 124°, and is converted by benzoyl chloride in pyridine into *β-benzoyl-α-diphenylethylhydrazine*, $NHBz\cdot NH\cdot CHPh\cdot CH_2Ph$, m. p. 144°. The chief product of the interaction of magnesium ethyl bromide and benzaldazine is benzaldehydebenzylhydrazone (Franzen and Deibel, *loc. cit.*); with an excess of the organo-magnesium bromide (4 mols.), however, the main products are those formed by the decomposition of the initially formed benzaldehydephenylpropylhydrazone, namely, benzaldehyde and

γδ-diphenylhexane. The reaction between anisaldazine and magnesium benzyl chloride leads to the formation of two *substances*, one having m. p. 84° (decomp.), the other decomposing at 99°; since both have the same properties and composition, and yield anisaldehyde by treatment with mineral acids, they are regarded as the stereoisomeric modifications of *methoxybenzaldehydemethoxydiphenylethylhydrazone*,

$$OMe\cdot C_6H_4\cdot CH{:}N\cdot NH\cdot CH(CH_2Ph)\cdot C_6H_4\cdot OMe.$$

C. S.

Opening of the Glyoxaline Ring. Adolf Windaus (*Ber.*, 1910, 43, 499—501).—Glyoxaline and its homologues, alkylated in the α- and β-positions, on treatment with benzoyl chloride and sodium hydroxide are converted into dibenzoyl derivatives of unsaturated diamines, but glyoxaline derivatives containing a free carboxyl group in the side-chain are stable towards these reagents. The stability is due to the presence of the free carboxyl group, as glyoxalylpropionanilide is very readily converted into an unsaturated diamino-acid.

Glyoxalylpropionanilide, $CH\ll^{NH\cdot CH}_{N-\!-C\cdot CH_2\cdot CH_2\cdot CO\cdot NHPh}$, formed by heating glyoxalylpropionic acid with aniline at 185°, forms short, prismatic crystals, m. p. 190—191°. The *oxalate* forms four-sided plates; the *picronolate*, long, light yellow needles; the *platinichloride* crystallises in bright orange, fork-like needles; the *silver* salt is colourless.

On heating with benzoyl chloride and potassium hydroxide, the ring is broken, and the *dibenzoyl* compound

$$COPh\cdot NH\cdot CH{:}C(NH\cdot COPh)\cdot CH_2\cdot CH_2\cdot CO\cdot NHPh$$

is formed, crystallising in long, lustrous needles, m. p. 197°.

E. F. A.

Action of 1-Chloro-2:4-dinitrobenzene on Pyridine Bases. Fritz Reitzenstein and Georg Stamm (*J. pr. Chem.*, 1910, [ii], 81, 160—166).—Phenanthroline or γ-dipyridyl reacts with 1-chloro-2:4-dinitrobenzene in boiling acetone to form an unstable substance, probably by the addition of 1 mol. of chlorodinitrobenzene to each of the nitrogen atoms; these additive compounds are isolated as the *platinichlorides*, $[C_{12}H_8N_2,2C_6H_3(NO_2)_2Cl],H_2PtCl_6$, m. p. above 300°, and $[C_{10}H_8N_2,2C_6H_3(NO_2)_2Cl],H_2PtCl_6$, sintering above 270°. When aniline is also present in the solution, the additive compound is not produced, 2:4-dinitrodiphenylamine being obtained by the interaction of the aniline and the chlorodinitrobenzene. C. S.

Quinazolines. XXIV. Oxalylanthranilic Compounds and Quinazolines Derived Therefrom. Marston T. Bogert and Ross A. Gortner (*J. Amer. Chem. Soc.*, 1910, 32, 119—128).—This paper gives an account of compounds derived from oxalylanthranilic acid, which was first obtained by Kretschy (Abstr., 1883, 674; 1884, 750). When methoxalyl- and ethoxalyl-anthranilic acids and oxalyldianthranilic acid (Mauthner and Suida, Abstr., 1889, 139) are heated with acetic anhydride, they are converted into acylanthranils, $\begin{matrix}C_6H_4\\CO-\!-\end{matrix}\!>N\cdot CO\cdot CO_2R$

and $\begin{matrix}C_6H_4\\CO\end{matrix}\!>\!N\cdot CO\cdot CO\cdot N\!<\!\begin{matrix}CO\\C_6H_4\end{matrix}$. Methoxalyl- and ethoxalyl-anthranil condense with primary amines to form the corresponding quinazolines, $C_6H_4\!<\!\begin{matrix}N{=}C\cdot CO_2R\\CO{-}NR'\end{matrix}$.

Methoxalylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2Me$, m. p. 176·5° (corr.), obtained together with some oxalyldianthranilic acid by heating anthranilic acid (1 mol.) with methyl oxalate (1 mol.) at 140—155°, forms colourless crystals. Ethoxalylanthranilic acid has m. p. 184° (corr.). Oxalyldianthranilic acid can be prepared by heating anthranilic acid (2 mols.) with ethyl oxalate (1 mol.), as stated by Mauthner and Suida (*loc. cit.*), or by the action of oxalyl chloride on the acid.

Methoxalylanthranil, $\begin{matrix}C_6H_4\\CO\end{matrix}\!>\!N\cdot CO\cdot CO_2Me$, m. p. 177·5° (corr.), forms light brown needles, and is readily hydrolysed by water. *Ethoxalylanthranil*, m. p. 129—130° (corr.), crystallises in large, colourless plates, and is more stable than the methyl derivative, but is rapidly hydrolysed by boiling water. *Oxalyldianthranil*, m. p. about 345° (uncorr.), forms a yellow powder, and is hydrolysed slowly by boiling water and rapidly by hot concentrated hydrochloric acid.

When ethoxalylanthranil is treated with alcoholic ammonia it is converted into *ammonium 4-quinazolone-2-carboxylate*, m. p. 229° (decomp.). *4-Quinazolone-2-carboxylic acid* (*4-hydroxyquinazoline-2-carboxylic acid*), $C_6H_4\!<\!\begin{matrix}N{=}C\cdot CO_2H\\CO{-}NH\end{matrix}$, forms white, silky needles, and melts at 230° (corr.) with evolution of carbon dioxide and formation of 4-quinazolone (4-hydroxyquinazoline), m. p. 214° (corr.). By heating ethoxalylanthranil with carbamide at 140—150°, *ethyl 4-quinazolone-2-carboxylate*, m. p. 185·5° (corr.), is produced. When ethoxalylanthranil (1 mol.) is heated with an aqueous solution of methylamine (2 mols.), *3-methyl-4-quinazolone-2-carboxymethylamide*,

$$C_6H_4\!<\!\begin{matrix}N{=}C\cdot CO\cdot NHMe\\CO{-}NMe\end{matrix},$$

m. p. 160° (corr.), is produced, which forms pale rose-coloured prisms. Methoxalylanthranil reacts with aniline to form *methyl 3-phenyl-4-quinazolone-2-carboxylate*, $C_6H_4\!<\!\begin{matrix}N{=}C\cdot CO_2Me\\CO{-}NPh\end{matrix}$, m. p. 203·5° (corr.), which crystallises in small, colourless plates. The corresponding *ethyl* ester, m. p. 160° (corr), is accompanied in its formation by *ethyl 4-phenylimino-3-phenylquinazoline-2-carboxylate*,

$$C_6H_4\!<\!\begin{matrix}N{=}\!=\!=C\cdot CO_2Et\\C(NPh)\cdot NPh\end{matrix},$$

m. p. 291° (decomp.), which forms a colourless, crystalline powder. *Ethyl 4-β-naphthylimino-3-β-naphthylquinazoline-2-carboxylate*, m. p. 253—254° (corr.), is similarly obtained as a grey, crystalline powder. When ethoxalylanthranil (1 mol.) is heated with phenylhydrazine (1 mol.), *ethyl 3-anilino-4-quinazolone-2-carboxylate*,

$$C_6H_4\!<\!\begin{matrix}N{=}C\cdot CO_2Et\\CO{-}N\cdot NHPh\end{matrix},$$

m. p. 142° (corr.), is produced, which forms long, lemon-yellow needles. By the action of hydrazine hydrate on ethoxalyl- or methoxalyl-anthranil, *s-bis-3-amino-4-quinazolone-2-carboxylic hydrazide*,

$$\left[C_6H_4<\begin{matrix}N=C\cdot CO\cdot NH\cdot\\ CO\cdot N\cdot NH_2\end{matrix}\right]_2,$$

m. p. 157—158° (corr.), is obtained as a yellow, amorphous solid. When this compound is boiled with concentrated hydrochloric acid, it is converted into *3-amino-2-carbazino-4-quinazolone*,

$$C_6H_4<\begin{matrix}N=C\cdot CO\cdot NH\cdot NH_2\\ CO\cdot N\cdot NH_2\end{matrix},$$

m. p. 202·5° (corr.), which crystallises in transparent plates; its *hydrochloride* has m. p. 190—191° (corr.), and its *diacetyl* derivative, $C_6H_4<\begin{matrix}N=C\cdot CO\cdot NH\cdot NHAc\\ CO\cdot N\cdot NHAc\end{matrix}$, has m. p. 125° (corr.). E. G.

Indanthren and Flavanthren. XII. Products of the Action of Nitric Acid on Flavanthren. Elementary Analysis of Difficultly Combustible Substances Rich in Carbon. Karl Holdermann and Roland Scholl (*Ber.*, 1910, **43**, 340—345. Compare Abstr., 1908, i, 696).—When flavanthren (Abstr., 1907, i, 540) is boiled for eight hours with a mixture of nitric acid, D 1·52, and concentrated sulphuric acid, at least three products are obtained, of which the least soluble has been examined. It is a yellow, microcrystalline powder of the composition $C_{28}H_8O_{10}N_6$, and appears to be a *dinitrodinitrosodihydroxyflavanthren*. It is unchanged by sulphurous acid, forms a black *potassium* derivative, yields *dinitrosodianilinodihydroxyflavanthren*, $C_{40}H_{20}O_6N_6$, when boiled with aniline, and is reduced by alkaline hyposulphite to the blue vat dye of *tetraaminodihydroxyflavanthren*; the latter is obtained by reduction with ammonium sulphide and ammonium hydroxide, and is a blue substance resembling indigo. It is again reduced by alkaline hyposulphite to the deep blue vat dye, which produces on unmordanted cotton bluish-black shades, turned green by hydrochloric acid, the original shade being restored by treatment with water.

The estimation of the carbon and the nitrogen in anthracene derivatives of high molecular weight, which may be several units % too low by the ordinary processes, may be accurately effected by the Dennstedt method or by modifications of the ordinary processes which are described by the author. C. S.

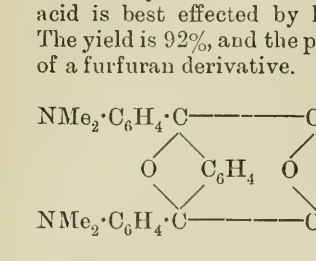
Addition Theory. Arthur Michael (*Ber.*, 1910, **43**, 621—627). —The conclusion is drawn that the results obtained by Acree, Johnson, Brunel, Shadinger, and Nirdlinger with urazoles (Abstr., 1908, i, 919) are in complete harmony with the author's theory of addition. Acree's investigations merely show that the laws of mass action hold good in the reactions between urazole salts and alkyl halides.

The views held by Acree on the mechanism of tautomeric changes are not based on experimental facts, and are untenable. J. J. S.

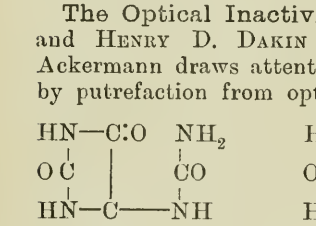
Phthaleins and Dibenzoylbenzenes. Alfred Guyot and Albin Haller (*Ann. Chim. Phys.*, 1910, [8], **19**, 297—353).—This paper

consists mainly of a résumé of previous communications, together with further experimental details (compare Abstr., 1898, i, 670; 1900, i, 170; 1901, i, 146, 270, 350; 1903, i, 348, 748; 1904, 83, 314, 659, 660; 1905, 188, 226, 270, 516, 540; 1906, i, 761; 1907, i, 76, 565; 1908, i, 569).

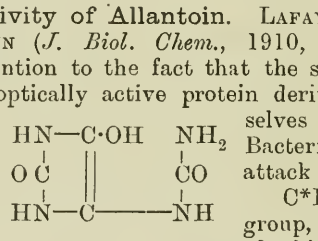
The dehydration of tetramethyldiaminotriphenylmethane-*o*-carboxylic acid is best effected by heating the substance with acetic anhydride. The yield is 92%, and the product probably has the annexed constitution of a furfuran derivative. Details are given for the preparation of tetramethyldiaminodibenzoylbenzene from the product. When the substance is heated with sulphuric acid, depolymerisation occurs, and a *compound*, $C_{24}H_{24}ON_2$, is obtained. This crystallises in orange-red prisms, m. p. 140°, showing an orange-yellow phosphorescence when heated, and readily reverting to the original substance. The action of sulphuric acid leads also to the formation of a higher polymeride, occurring as a pale yellow, crystalline mass. W. O. W.



The Optical Inactivity of Allantoin. Lafayette B. Mendel and Henry D. Dakin (*J. Biol. Chem.*, 1910, 7, 153—156).—Ackermann draws attention to the fact that the substances derived by putrefaction from optically active protein derivatives are themselves optically inactive. Bacteria are prone to attack the $C^*H(NH_2)\cdot CO_2H$ group, and the removal of this group abolishes molecular asymmetry. Allantoin, however, contains an asymmetric carbon atom according to the accepted formula, but no examination of its actual behaviour has yet been made. Allantoin of urinary origin was found to be inactive. An attempt to effect a resolution of the inactive substance by bacterial action failed. Several possibilities are discussed to explain the inactivity: the one most favoured is that allantoin exhibits tautomerism; thus it may be represented by the two annexed formulæ: the first is the usual one, whilst the second contains no asymmetric carbon atom. W. D. H.



(I.)



(II.)

Influence of Hydroxyl Ions on Azo-coupling. II. Gustav Heller [with Wilhelm E. Galleh] (*J. pr. Chem.*, 1910, [ii], 81, 184—187. Compare Abstr., 1908, i, 300).—Solutions of benzenediazonium chloride (1 mol.), prepared in the usual way, are added to aqueous solutions of phenol (1/3 mol.) containing sodium hydroxide ($1\frac{5}{6}$ mol.), together with 20, 40, 70, or 100 grams excess of the alkali. The amount of bisbenzeneazophenol increases slowly, but continuously, that of trisbenzeneazophenol decreases very largely and rapidly, as the concentration of the alkali increases. The by-products are regarded as

O-azo-compounds, since by prolonged heating with alcohol they are converted into bis- and tris-benzeneazophenol. The conversion of the *O*-azo-compounds into real azo-compounds appears to be retarded by an excess of alkali. C. S.

Action of Heat on *o*-Aminoazo-compounds. G. Charrier (*Atti R. Accad. Sci. Torino*, 1910, **45**, 131—139).—On heating at about 300°, *o*-aminoazo-compounds decompose into triazole, primary amine, and ortho-diamine. This decomposition supports the formula $NH_2{\cdot}Ar{\cdot}N{:}NAr'$ for the *o*-aminoazo-compounds, and is represented by the equation :

$$3NH_2{\cdot}Ar{\cdot}N{:}NAr' = 2Ar\langle\overset{N}{\underset{N}{|}}\rangle NAr' + NH_2Ar' + Ar(NH_2)_2.$$

Thus, tolueneazo-*p*-toluidine yields 2-*p*-tolyl-5-methyl-2 : 1 : 3-benztriazole (compare Zincke, Abstr., 1886, 236), *p*-toluidine, and tolylene-3 : 4-diamine. Benzeneazo-β-naphthylamine gives phenylnaphthatriazole (compare Zincke, *loc. cit.*), aniline, and 1 : 2-naphthylenediamine.

p-*Tolueneazo-β-naphthylamine*, $NH_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4Me$, prepared by the action of *p*-toluenediazonium chloride on β-naphthylamine, forms red needles, m. p. 113°. When heated at 300° it decomposes into *p*-toluidine, 1 : 2-naphthylenediamine, and 2-p-*tolylnaphthatriazole*, $C_{10}H_6\langle\overset{N}{\underset{N}{|}}\rangle N{\cdot}C_6H_4Me$, which crystallises in slender, white needles, m. p. 148—149°, and gives a greenish-brown solution in concentrated sulphuric acid. T. H. P.

The Proteins. I. Behaviour of Protein Solutions with Acetone. Theodor Weyl (*Ber.*, 1910, **43**, 508—511).—Having found that many proteins are precipitated from their solutions by acetone, the author has applied the property to the estimation of the proteins in cow's milk and in fresh bullock's blood, and obtains concordant results. The milk or the blood is diluted with an equal volume of water, and poured into 4 vols. of acetone. The precipitate is collected, washed with equal volumes of acetone and water, then with alcohol, and is finally extracted with ether in a Soxhlet apparatus, dried, and weighed. C. S.

The Isoelectric Constants and the Relative Acidity Constants of Serum-Albumin. Leonor Michaelis and B. Mostynski (*Biochem. Zeitsch.*, 1910, **24**, 79—91).—From its amphoteric character it can be theoretically deduced from the laws of mass action that the sum of the protein ions is a minimum when the acidity of the solution represents the isoelectric point. This condition can be represented by the equation : $k_a/k_b = [H']^2/k_w$, where k_a and k_b are the dissociation constants of the protein, functioning respectively as acid and base, and k_w is the dissociation constant of water. This point was experimentally determined by ascertaining the point at which the protein wandered neither to the anode nor cathode in an apparatus arranged according to the following scheme :

Copper in cupric chloride	"Acid mixture" without protein	Acid mixture with 1% protein	Acid mixture without protein	Silver in sodium chloride

The acid mixture was in one set of experiments varying proportions of primary and secondary phosphates, and in the second set, varying proportions of acetic acid and sodium acetate. The isoelectric point was found in one case when the relative amounts of primary to secondary phosphate were as 50 : 1 or $H = 1{\cdot}4\ 10^{-5}$, and in the other case, where the ratio of acetic acid to sodium acetate was between 1 : 2 and 3 : 7 or $H = 1{\cdot}08 \times 10^{-5}$ and $0{\cdot}85\ 10^{-5}$. The above results were obtained with unheated albumin. With heated albumin it was observed that coagulation rapidly took place when the hydrogen ion concentration was near the isoelectric point. The optimum condition for coagulation could be determined with great accuracy, using either of the "acid mixtures" mentioned above. It was found to take place when $[H'] = 0{\cdot}82 \times 10^{-5}$. Theoretical reasons are deduced for believing that the optimum conditions for coagulation correspond with the isoelectric point. From these results it is calculated that the relative acidity constant for ox-serum at 18° is $1{\cdot}1 \times 10^{-4}$. S. B. S.

Putrefaction of Lysine-free Protein. D. Ackermann (*Zeitsch. physiol. Chem.*, 1910, **64**, 91—94).—Previous experiments have shown that there is reason to believe that arginine is the parent substance of tetramethylenediamine and δ-aminovaleric acid, and that lysine is the parent substance of pentamethylenediamine. On the addition of lysine to a putrefying mixture, the yield of pentamethylenediamine is increased. The present experiments now show that in the putrefaction of gliadin, which is a protein free from lysine, there is no formation of pentamethylenediamine. W. D. H.

The Nature of Oxyhæmoglobin. Joseph Barcroft and A. V. Hill (*J. Physiol.*, 1910, **39**, 411—428).—The velocity of dissociation of oxyhæmoglobin obeys an equation derived from the laws of mass action, and has a high temperature-coefficient, increasing about four times for a rise of 10°. The variations of the equilibrium constant K with change of temperature T follow the equation $\frac{1}{K} \cdot \frac{dK}{dT} = \frac{-q}{2T^2}$, where q is constant and equal to 28,000 calories. From the second law of thermodynamics, q is the heat of combination of 1 gram-molecule of hæmoglobin with oxygen. The amount of heat given out when 1 gram of hæmoglobin unites with oxygen is 1·85 calories. The least possible value for the molecular weight of hæmoglobin in dialysed solution is 16,669. The general conclusion is that hæmoglobin unites chemically with oxygen according to the formula : $Hæm. + O_2 \rightleftarrows Hæm.O_2$, and that it is not an adsorption phenomenon. W. D. H.

Modification of Fischer's Ester Method. B. O. Pribram (*Monatsh.*, 1910, **31**, 51—54).—Dry ammonia is employed to liberate the esters of amino-acids from their hydrochlorides. In a preliminary trial, 10 grams of ethyl glycine hydrochloride, dissolved in the smallest necessary quantity of absolute alcohol, were treated with dry ammonia, and, after the addition of dry ether and removal of the ammonium chloride, the solution was evaporated under diminished pressure, the ester was redissolved in alcohol, and the hydrochloride regenerated by

hydrogen chloride; its weight was 6·9 grams, or 69% of the original quantity.

The applicability of the process to the isolation of the products of the hydrolysis of a protein is defined by the following experiment. Dry gelatin is hydrolysed by concentrated hydrochloric acid, the glutamic acid hydrochloride is removed in the usual way, and the filtrate is evaporated to a syrup, which is esterified by the ordinary process of Fischer. After the removal of the ethyl glycine hydrochloride, the filtrate is concentrated under diminished pressure, mixed with dry ether, and saturated with dry ammonia; after about ten minutes, the ether is poured off, replaced by fresh dry ether, and the current of ammonia passed anew, the processes being repeated until the ether remains colourless. The combined ethereal solutions can be directly fractionated, whilst the other products of the hydrolysis can be extracted from the paste of ammonium chloride by means of alcohol. In this way 400 grams of gelatin yield 119·3 grams of esters, whereas by Fischer's process of liberating the esters from the hydrochlorides, 500 grams of gelatin give 117 grams of esters. C. S.

Course of the Hydrolysis of Proteins by Aqueous or Alcoholic Hydrogen Chloride. M. Pfannl (*Monatsh.*, 1910, **31**, 81—85).—Pribram (preceding abstract) has observed that the amount of glycine obtained by the hydrolysis of gelatin by alcoholic hydrogen chloride is very much smaller than that produced when the hydrolysis is effected by hydrochloric acid, and also that the quantities of the esters of amino-acids richer in carbon are about the same in the two processes of hydrolysis. The author now finds that, if care is taken to prevent the hydrolysis of the easily decomposable glycine ester, gelatin yields qualitatively and quantitatively the same products whichever method of hydrolysis is employed. The same is true of the hydrolysis of silk fibroin. C. S.

Comparative Investigations on the Composition and Cleavage of Different Kinds of Silk. VIII. The Mono-amino-acids from Tai-Tsao-Tsam Silk (China). Emil Abderhalden and Julius Schmid. **IX. The Mono-amino-acids from Chefoo Silk.** E. Abderhalden and Ernst Welde (*Zeitsch. physiol. Chem.*, 1910, **64**, 460—461, 462—463).—The following table shows the amount of amino-acids in grams per cent. of the two varieties of silk investigated:

	Tai-Tsao-Tsam silk.	Chefoo silk.
Glycine	25·2	12·5
Alanine	18·2	18·0
Leucine	0·9	1·2
Serine	1·2	1·0
Aspartic acid	2·1	2·0
Glutamic acid	2·0	2·0
Phenylalanine	1·0	1·0
Tyrosine	7·8	8·5
Proline	1·0	2·5

W. D. H.

Cataphoresis of Ferments and Colloids. Henri Iscovesco (*Biochem. Zeitsch.*, 1910, 24, 53—78).—The experiments were carried out in an apparatus, which is figured in the text, consisting essentially of a combination of U-tubes with a central part, which can be shut off from the remainder by glass taps, into which the substance under investigation is introduced. In investigating enzymes, this substance is coagulated egg-white or gelatin, the remainder of the apparatus being filled with enzyme solution. By this arrangement the distance between the electrodes, by means of which the current is introduced, is great, and the effect of electrolysis can be practically eliminated. By determining on which side the ovalbumin or gelatin undergoes alteration, conclusions can be drawn as to the behaviour of the enzymes in an electrical field. By choosing a sufficiently low potential and current strength, appreciable destruction of the enzyme can be avoided. Pepsin wanders towards the negative pole, passes through the ovalbumin on the positive side, and digests it; this can happen before destruction of the enzyme takes place; the latter is affected chiefly by the amount of energy employed (expressed in watts). Similar results with regard to ferment destruction were obtained by the catalase of pigs' liver, which wanders towards the anode. Arsenious sulphide wanders through hardened gelatin towards the positive pole. Similar experiments were performed with colloidal iron, silver, and Magdala-red, and coagulated blood-serum. The result in the last-named case indicated the presence of electropositive and electronegative albumins in the serum. S. B. S.

The Kinetics of Enzyme Actions. Sven G. Hedin (*Zeitsch. physiol. Chem.*, 1910, 64, 82—90. Compare Abstr., 1909, i, 73).—The experiments recorded with trypsin and rennet show that the law of enzyme action is frequently nullified by the presence of inhibiting substances either in the preparation of the enzyme or in the substrate. W. D. H.

The Question of the Identity of Pepsin and Rennet. W. van Dam (*Zeitsch. physiol. Chem.*, 1910, 64, 316—330).—From the experiments described, it is held that there is no ground for distinguishing a proteolytic from the milk curdling enzyme of the gastric juice. By altering various factors, sometimes the one, sometimes the other action becomes predominant, and the bulk of the paper is concerned with variations in the conditions which lead to such results. W. D. H.

The Enzymes of Gum Acacia. Friedrich Reinitzer (*Zeitsch. physiol. Chem.*, 1910, 64, 164—168. Compare Abstr., 1909, i, 751). —Polemical. A reply to criticisms by Grafe (this vol., i, 148). W. D. H.

New Observations on the Individuality of Cellase. Gabriel Bertrand and Maurice Holderer (*Compt. rend.*, 1910, 150, 230—232. Compare this vol. i, 212).—Evidence is adduced in support of the existence of a specific ferment, *cellase*, capable of

effecting the hydrolysis of cellose. The new diastase has been recognised in apricot seeds, in the grains of barley, and in the mycelium of *Aspergillus niger*. It does not appear to occur in blood-serum of horses, in top fermentation yeast, or in glycerol macerations of *Russula queletii*. Partial separation of cellase from emulsin can be effected by taking advantage of the different rates at which the enzymes filter through porcelain. W. O. W.

Method for the Rapid Preparation of Oxidising Enzymes from Plant Extracts. Alexis Bach (*Ber.*, 1910, 43, 362—363).—The addition of 5—10% of magnesium sulphate to a plant extract has the effect of so changing the colloid substances present that they can be easily and quickly precipitated by relatively small quantities of alcohol. Thus, from the extract of *Russula delica*, 5% of magnesium sulphate, followed by alcohol until the solution contained 48%, caused the precipitation of the major part of the impurities. The further addition of alcohol until 70—75% was present, precipitated light-coloured, crystalline substances very rich in oxydases, the last fraction being mainly tyrosinase. The fractions may be freed from magnesium sulphate by dialysis against running water. The precipitates settle rapidly, and the whole process only takes three to four hours. E. F. A.

Theory of the Action of Oxydases. I. Oxydases free from Manganese and Iron. Alexis Bach (*Ber.*, 1910, 43, 364—366).—Bertrand (Abstr., 1898, i, 53; ii, 128) has suggested that oxydases are to be regarded as organic manganese compounds. Others have prepared active oxydases containing iron instead of manganese, whilst the peroxydases (Bach and Tscherniac, Abstr., 1908, i, 746) have been proved to contain neither metal. Active oxydase preparations have now been obtained from *Lactarius vellereus* and *Russula delica* by precipitation with 65—75% alcohol, after the addition of magnesium sulphate (see preceding abstract), which are absolutely free from either manganese or iron. E. F. A.

Theory of the Action of Oxydases. II. Influence of Metallic Salts on the Subsequent Change of the Products of Oxydase Action. Alexis Bach (*Ber.*, 1910, 43, 366—370).—Metallic salts do not take part in the primary oxidation of tyrosine and phenols by tyrosinase or phenolase, that is, the absorption and activation of the oxygen, but they very greatly accelerate the further change of the primary oxidation products. Thus a tyrosine solution coloured deep red by the action of tyrosinase becomes violet and then black in a few minutes on the addition of aluminium sulphate, and the characteristic black precipitate soon forms. Aluminium sulphate similarly accelerates the formation of purpurogallin from the yellow product formed by the action of oxydase on pyrogallol.

Metallic salts also indirectly accelerate the actual oxydase action when they facilitate the removal of products of the action which are acting to stop the oxydase. This explanation applies to the accelerating action of manganese salts on the oxidation of drying oils and

quinol. Oxydase action is to be regarded as a process taking place in two phases, and brought about by the agency of two kinds of catalyst. The molecular oxygen is activated by the oxygenase, forming peroxide, whilst the peroxydase brings about the transference of the labile peroxide oxygen to the substrate. In the case of phenolase, the peroxydase can be replaced by metallic salts, but with tyrosine the metallic salts are not replaceable by peroxydase. E. F. A.

Formation of Phosphates in Alcoholic Fermentation. Arthur Harden and William J. Young (*Centr. Bakt. Par.*, 1910, ii, 26, 178—184. Compare Abstr., 1908, i, 590).—The formation of hexose phosphate is accompanied by an exactly equivalent amount of alcoholic fermentation, and does not precede the alcoholic fermentation as required by Iwanoff's theory (Abstr., 1909, i, 752).

The loss of fermenting power caused by washing zymin with water is shown to be due to the removal of the soluble co-enzyme. There is no experimental evidence that Iwanoff's synthease exists.

N. H. J. M.

Transformation of Aromatic Alcohols into Phosphinous Acids by Hypophosphorous Acid. Robert Fosse (*Compt. rend.*, 1910, 150, 178—180; *Bull. Soc. chim.*, 1910, [iv], 7, 228—231. Compare Abstr., 1906, i, 691, 975; 1907, i, 414; 1908, i, 567).—Certain aromatic alcohols react with hypophosphorous acid with the elimination of water and the formation of a substituted acid; simultaneously, a portion of the alcohol undergoes reduction to the corresponding hydrocarbon. Thus triphenylcarbinol forms triphenylmethane and *triphenylmethylphosphinous acid*, $CPh_3 \cdot PHO \cdot OH$. Dinaphthapyranol forms dinaphthapyran and *dinaphthapyrylphosphinous acid*, $O<^{C_{10}H_6}_{C_{10}H_6}>CH \cdot PHO \cdot OH$ Michler's carbinol forms the corresponding hydrocarbon and the *acid*, $CH(C_6H_4 \cdot NMe_2)_2 \cdot PHO \cdot OH$.

When the corresponding aldehydes or ketones are treated with hypophosphorous acid, additive compounds are formed of the type $R \cdot CH(OH) \cdot PHO \cdot OH$. W. O. W.

Preparation of an Arsenic-albumin Compound. Friedr. August Volkmar Klopfer (D.R.-P. 214717).—When the nuclein-free vegetable albumin obtained from wheat is treated with arsenious chloride in the presence of a diluting agent, reaction takes place at the ordinary temperature. The *arseno-albumin* so obtained is readily soluble in water, but insoluble in the gastric juice; it contains N = 12·95%, S = 1·78%, Cl = 4·72%, and As = 4·33%. F. M. G. M.

Organic Chemistry.

Some Fluoro-derivatives of Methane. Frédéric Swarts (*Bull. Acad. roy. Belg.*, 1910, 113—123).—When bromoform (3 mols.) is heated with antimony trifluoride and bromine in a platinum reflux apparatus for twenty-four hours at 110—120°, one atom of bromine is substituted by fluorine. If double the proportion of antimony trifluoride is used and the heating continued for seventy-two hours, two atoms of bromine are replaced, but the latter reaction does not occur to any appreciable extent until the former is complete.

Fluorodibromomethane, $CHFBr_2$, the product of the first reaction, is a colourless liquid, b. p. (corr.) 64·9°/757 mm., $D^{18\cdot5}$ 2·4256, which becomes slightly yellow when exposed to the light. It is slowly decomposed on exposure to light and moist air, with the formation of hydrogen fluoride and bromide. Fluorodibromomethane is reduced by zinc dust in alcoholic solution at 70° with the production of methylene fluorobromide, methyl fluoride, and hydrogen. That the latter is formed by the catalytic dehydrogenation of the alcohol is shown by the presence of aldehyde in the alcoholic solution. Fluorodibromomethane is attacked by sodium ethoxide with the formation of sodium formate.

Difluorobromomethane, $CHBrF_2$, the product of the second of the above reactions, is a gas, b. p. −14·5°, $D^{15\cdot7}$ 4·53—4·57 (air = 1), soluble in half its volume of water at 18°, and in one-thirty sixth of its volume of alcohol at 17°. When passed over soda-lime it is decomposed, approximately two-fifths being converted into carbon monoxide, and the remainder into formate. The reaction, very rapid at first, about 70% of the total change occurring in the first thirty minutes, afterwards slackens, and requires nine days for completion. Concentrated aqueous potassium hydroxide solutions act similarly. An ethereal solution of difluorobromomethane is not attacked by sodium at the ordinary temperature. When an absolute alcoholic solution of the gas (1 mol.) at −15° is treated with a solution of potassium ethoxide (1 mol.) in the same solvent at the same temperature, the product consists of unchanged substance, potassium formate, slight amounts of potassium fluoride and bromide, and a small quantity of a *liquid*, b. p. 45—50°, insoluble in water, which seems to be ethyl difluoromethyl ether, $CHF_2{\cdot}OEt$, isomeric with the difluoroethyl methyl ether described previously (Abstr., 1902, i, 129). An attempt to replace the hydrogen atom in difluorobromomethane by mercury by treatment with an alkaline solution of mercuric cyanide was also unsuccessful.

It has been shown previously (Abstr., 1898, i, 457) that the replacement of bromine by fluorine in the halogen compounds containing C_2 causes a depression in the boiling points of about 63°. It is now found that in the methane series the corresponding

depression is almost constantly 80°. The corresponding lowering of the boiling points of the chloro-derivatives by substitution of fluorine is about 44° in compounds containing C_2, and 50° in the methane series respectively. E. H.

Non-dehydration of Hydrates by Absolute Alcohol. Frans A. H. Schreinemakers (*Chem. Weekblad*, 1910, 7, 211—216).—Absolute alcohol extracts the water of crystallisation from the hydrates $BaCl_2,H_2O$; $BaCl_2,2H_2O$, and $Li_3SbS_4,10H_2O$, but not from $CuCl_2,2H_2O$ and $CuSO_4,H_2O$. A. J. W.

Mechanism of Catalytic Dehydration of Alcohols by Different Metallic Oxides. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1910, 150, 823—826. Compare Abstr., 1908, i, 594, 713; 1909, i, 546).—The following equations are put forward to account for the catalytic dehydration of alcohols by thorium oxide: (1) $ThO_2 + 2C_nH_{2n+1}\cdot OH = ThO(OC_nH_{2n+1})_2 + H_2O$. (2) Below 300°: $ThO(OC_nH_{2n+1})_2 = ThO_2 + (C_nH_{2n+1})_2O$. (3) Above 300°:

$$ThO(OC_nH_{2n+1})_2 = ThO_2 + H_2O + 2C_nH_{2n}.$$

The catalytic formation of amines (Abstr., 1909, i, 292) may similarly be explained by the interaction of the unstable thorate and ammonia. It might be expected that the action of hydrogen sulphide on the thorate would lead to the formation of thiols; experiments have verified this prediction, and led to the discovery of a new general method for the synthesis of these substances. W. O. W.

Autoxidation of Aliphatic Amino- and Polyhydroxy-derivatives. Wilhelm Traube (*Ber.*, 1910, 43, 763—772).—It has been shown previously that aqueous solutions of amines and amino-acids are capable of dissolving copper powder in the presence of oxygen, the products being aldehydes and ammonia (Abstr., 1906, i, 143). It is now shown that aqueous solutions of polyhydroxy-compounds, such as ethylene glycol, glycerol, or mannitol, are capable of dissolving copper in the presence of oxygen, and that the product of oxidation in each case is formic acid. It has been proved that carbonic acid is not formed during the oxidation. The absorption of oxygen takes place more rapidly when copper wool is used in place of turnings.

Oxygen is also absorbed when an alkaline solution of cupric hydroxide is used instead of metallic copper, but in this case it is advisable to work at a temperature of 60—70°.

Fehling's solution also absorbs oxygen, yielding formic acid. Solutions of cupric hydroxide in methylamine or in alkaline solutions of glycine absorb oxygen at 60°, yielding formaldehyde in the first case and oxalic acid in the second.

In all these reactions, the absorption of oxygen and the oxidation of the ammonia, amine, or hydroxy-compound proceed more readily when metallic copper is present and goes into solution. If cupric hydroxide is used, a higher temperature is required. This may be due to the fact that the oxidation and solution of the copper produce

local raising of the temperature, which accelerates the oxidation of the organic compound; when a solution of copper hydroxide is used, no internal heating takes place, and hence the need of external heating.

In all cases the reaction is regarded as an oxidation of complex copper compounds, for example, with ammonia of the compound

$$Cu(NH_3)_2(OH)_2,$$

and in all cases a certain minimum concentration of hydroxyl ions is necessary. It is possible that the copper of the complex compound takes up oxygen, yielding a copper peroxide derivative, and that the oxygen is then transferred to the amino- or hydroxy-portion of the complex molecule. J. J. S.

[Oxidation of Unsaturated Compounds by means of Organic Peroxides.] Nikolaus Prileschéeff (*Ber.*, 1910, 43, 959. Compare this vol., i, 86).—A reply to Lippmann's claim for priority (this vol., i, 149). C. S.

Organic Compounds Spontaneously Oxidisable with Phosphorescence. Marcel Delépine (*Compt. rend.*, 1910, 150, 876—878. Compare Abstr., 1902, i, 271, 595, 597, 702; 1903, i, 237).—Dithiocarbonic esters of the type OR·CS·SR′, and thiocarbamic esters of the type NR_2·CS·OR′, fume in the air at the ordinary temperature, emitting vapours which appear luminous in the dark. The ester, $CS(OMe)_2$, shows the same phenomenon. Phosphorescence, which is due to oxidation, varies in a marked manner with the volatility of the compounds, those members of the series having relatively low boiling points being the most luminous. The phosphorescence appears to be associated with the presence of the S:C·O− group in the molecule. W. O. W.

Lipoids. IX. Sahidin from Human Brain. Siegmund Fränkel and Kurt Linnert (*Biochem. Zeitsch.*, 1910, 24, 268—276).—The substance to which the authors give the name sahidin was prepared in the following way. To the concentrated extract made with light petroleum was added alcohol to precipitate the kephalin. After concentration, alcoholic lead acetate, made weakly alkaline with ammonia, was added. The excess of ammonia was distilled off, and the excess of lead precipitated by alcoholic hydrogen chloride, the latter being added until the solution was just acid to Congo paper. Cadmium chloride in alcoholic solution was then added, and the precipitate thus formed was extracted with hot benzene; from the latter solution, the cadmium salt of sahidin was precipitated, and was purified, after washing with alcohol, ether, and cold benzene, by solution again in hot benzene, and re-precipitation by alcohol. The analysis corresponds with the formula $C_{80}H_{167}O_{12}N_3Cl_6P_2Cd_3$. The substance is dextrorotatory andunsaturated (iodine number 34), and has only one methyl group combined with nitrogen. Only one atom of nitrogen, therefore, is in the form of choline, which was isolated both by acid hydrolysis and hydrolysis by barium hydroxide; a lævorotatory glycerophosphoric acid was also produced from the substance by hydrolysis. S. B. S.

A Comparison between the Properties of Protagon and the Properties of a Mixture of Phosphatides and Cerebrosides. Wilhelm Cramer (*Quart. J. exp. Physiol.*, 1910, 3, 129—138).—Polemical. W. D. H.

Ferriacetates, the Acetic Acid Reaction with Ferric Chloride, and the Basic Precipitation of Iron. Rudolf F. Weinland and Ernst Gussmann (*Zeitsch. anorg. Chem.*, 1910, 66, 157—168. Compare Abstr., 1909, i, 757).—A solution of ferric chloride (1 mol.) and sodium acetate (3 mols.) contains the hexa-acetotriferri-base previously described, the platinichloride of which is precipitated on the addition of sodium platinichloride. The red colour of such a solution is due to the presence of the mono-acetate, $\left[\begin{matrix}Fe_3(OAc)_6\\(OH)_2\end{matrix}\right]\cdot OAc$, and not to that of an undissociated acetate, $Fe(OAc)_3$. It has not been found possible to prepare a triacetate of the base.

The precipitate obtained when a solution containing ferric chloride and sodium acetate is boiled, corresponds approximately with the composition: $\left[\begin{matrix}OAc\\Fe_3\ (OH)_2\\O_3\end{matrix}\right]$.

The diacetate of the triferri-base is most readily prepared by dissolving the mono-acetate in hot glacial acetic acid, and distilling off the acetic acid at 130—140°. The salt forms rectangular, brick-red tablets. C. H. D.

Compounds with a Branched Chain. Mlle. Germaine Freylon (*Ann. chim. Phys.*, 1910, [viii], 19, 551—574).—Henri (*Jahresberichte*, 1889) has described the preparation of ethyl α-cyano-γ-methylvalerate by the action of *iso*butyl bromide on ethyl sodiocyanoacetate; repetition of his experiments, however, has shown that the sole product of the reaction is *ethyl α-cyano-γ-methyl-α-isobutylvalerate*, $C_{13}H_{23}O_2N$, b. p. 132°/15 mm. An unexpected result follows when this substance is reduced with sodium and absolute alcohol, three compounds being obtained: (1) *α-iso*butylvaleric acid; (2) *δ-methyl-β-isobutylamylamine*, $CH_2Pr^{\beta}\cdot CH(CH_2Pr^{\beta})\cdot CH_2\cdot NH_2$, b. p. 85—86°/18 mm.; the *carbamide* has m. p. 84—85°; the *phenylcarbamide* has m. p. 123°; (3) *α-cyano-γ-methyl-α-isobutylvaleric acid*, $CO_2H\cdot C(CH_2Pr^{\beta})_2\cdot CN$, m. p. 90—91°; when this is heated, carbon dioxide is lost, and *γ-methyl-α-isobutylvaleronitrile*, $CH(CH_2Pr^{\beta})\cdot CN$, is formed. The latter has b. p. 90—91°/15 mm., D_0^4 0·825; reduction leads to the formation of the foregoing amine, and when the substance is heated at 140° with sodium and the product treated with water, *βζ*-dimethylheptane is formed, together with di*iso*butyl ketone. The ketone, which has also been prepared from di*iso*butylcarbinol, forms a *semicarbazone*, m. p. 116—117°, and an *oxime*, b. p. 104—106°/10 mm., the *carbanilide* of which has m. p. 91—92°. Di*iso*butylcarbinol, b. p. 81—82°/18 mm., has not hitherto been obtained pure (Grignard, Abstr., 1901, i, 250); it forms a *phenylurethane*, m. p. 61—62°, and a *pyruvate*, b. p. 118—120°/18 mm., the *semicarbazone* of which has m. p. 114—115°. W. O. W.

Fatty Acids in Cod Liver Oil. A. Heiduschka and E. Rheinberger (*Pharm. Zentr.-h.*, 1910, 51, 203—204).—A solution in chloroform of the fatty acids, obtained by hydrolysing cod liver oil from the torsk with alcoholic potassium hydroxide and subsequent acidification, is treated with Hübl's iodine solution and kept in darkness for two days, whereby a sparingly soluble crystalline *powder*, $C_{17}H_{26}O_2Cl_4I_4$, is obtained, which is probably a derivative of terapic acid. Submitted to the action of dry chlorine at about 50° for ten hours, the powder is converted into an *octachloride*, $C_{17}H_{26}O_2Cl_8$, m. p. 62°. C. S.

Preparation of Glycerol Mono- and Di-lactates. Kalle & Co. (D.R.-P. 216917).—*Glycerol monolactate* is formed when an adequate mixture of glycerol and lactic acid is slowly heated to 150—160° and the product distilled in a vacuum; it is a viscous, colourless, hygroscopic syrup. *Glycerol dilactate* is prepared in the same way, and has similar properties; these compounds are also obtained when sodium, potassium, or silver lactate is heated with dichlorohydrin; they are sparingly soluble or insoluble in organic solvents; miscible with water or alcohol, in which they decompose slowly at the ordinary temperature, rapidly on heating; and are employed therapeutically as lactic acid substitutes. F. M. G. M.

Etholides from Coniferæ. Juniperic and Sabinic Acids. J. Bougault (*Compt. rend.*, 1910, 150, 874—876.* Compare Abstr., 1909, i, 82).—The constitution of juniperic and sabinic acids, recently obtained from the waxes of certain Coniferæ, has now been established. Sabinic acid is λ-hydroxylauric acid, since its iodo-derivative yields lauric acid on reduction, whilst oxidation of the acid gives Noerdlinger's decamethylenedicarboxylic acid (Abstr., 1890, 1237). Similarly, juniperic acid is *o*-hydroxypalmitic acid, since palmitic acid was obtained by reducing the iodo-derivative, and oxidation gave a tetradecamethylenedicarboxylic acid, identical with Canzoneri's thapsic acid (Abstr., 1883, 460).

The following derivatives are described: *o-iodopalmitic acid*, $CH_2I\cdot[CH_2]_{14}\cdot CO_2H$, m. p. 76°; *λ-iodolauric acid*, $CH_2I\cdot[CH_2]_{10}\cdot CO_2H$, m. p. 63—64°; *ethyl tetradecamethylenedicarboxylate*, $CO_2Et\cdot[CH_2]_{14}\cdot CO_2Et$, m. p. 39°. W. O. W.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc. II. Preparation of Aliphatic Ketonic Acids. I. Edmond É. Blaise and A. Kœhler (*Bull. Soc. chim.*, 1910, [iv], 7, 215—227).—An account, with further experimental details, of compounds obtained by the methods already described (Abstr., 1909, i, 204).

Ethyl hydrogen adipate, $C_8H_{14}O_4$, is crystalline, and has m. p. 29°, b. p. 160°/7 mm., 180°/19 mm.; the *anilide*, prepared from the acid chloride, crystallises in needles, m. p. 45°; the *α-naphthylamide* forms slender needles, m. p. 75°. The *chloride*, $CO_2Et\cdot[CH_2]_4\cdot COCl$, has b. p. 117—118°/9 mm., 128°/17 mm.

* and *J. Pharm. Chim.*, 1910, [vii], 1, 425—432.

Ethyl hydrogen pimelate, $C_9H_{16}O_4$, has m. p. 10°, b. p. 182°/18 mm., and forms a p-*toluidide*, m. p. 92°, and a *chloride*, b. p. 139°/17 mm.; diethyl pimelate has b. p. 144°/16 mm.

Ethyl hydrogen suberate, $C_{10}H_{18}O_4$, occurs in spherular crystals, m. p. 25°, b. p. 192°/17 mm., and forms a p-*toluidide*, m. p. 74°, and a *chloride*, b. p. 143°/15 mm.

ε-Ketoheptoic acid, prepared by treating ethyl adipyl chloride with zinc methyl iodide (compare Perkin, Trans., 1890, 57, 229), forms a *semicarbazone*, m. p. 144°; the *ethyl* ester, b. p. 120·5°/11 mm., forms a *semicarbazone*, m. p. 107°.

ε-Keto-octoic acid, m. p. 52°, b. p. 160—161°/9 mm., gives a green *copper* salt, a crystalline *calcium* salt, $C_{16}H_{26}O_6Ca,H_2O$, and a *semicarbazone*, m. p. 190°; the *methyl* ester has b. p. 122—123°/14 mm.; the *ethyl* ester, b. p. 125°/12 mm., forms a *semicarbazone*, m. p. 88·5°.

ε-Ketononoic acid gives a *copper* salt, a *potassium* salt,

$$C_9H_{15}O_3K,8H_2O,$$

a *semicarbazone*, m. p. 169°, and a *methyl* ester, b. p. 143°/21 mm.; the *ethyl* ester, b. p. 153°/21 mm., forms a *semicarbazone*, m. p. 85°.

The *nickel*, *mercury*, *potassium*, and *lead* salts of η-ketodecoic acid, m. p. 64°, are described; the *semicarbazone* has m. p. 184°; the *ethyl* ester, b. p. 157°/15 mm.

γ-Keto-octoic acid, m. p. 53°, furnishes a *semicarbazone*, m. p. 153°, a p-*nitrophenylhydrazone*, m. p. 152°, a *methyl* ester, b. p. 111°/15 mm., an *ethyl* ester, b. p. 125°/15 mm., and *copper*, *calcium*, and *zinc* salts, the two latter crystallising with $1H_2O$. W. O. W.

Some Derivatives of Mesoxalic Acid. H. Filippo, jun. (*Rec. trav. chim.*, 1910, [ii], 14, 113—129).—Sodium tartronate is conveniently obtained by heating sodium dihydroxytartrate to 100—120°. *Methyl tartronate* has m. p. 44·5—45°, and b. p. 122°/19 mm. Ethyl tartronate has m. p. 2·5° and b. p. 120·5—121°/15 mm. At atmospheric pressure the substance cannot be distilled without decomposition; this explains the contradictions found in the literature as to its b. p. *Tartronodi-methylamide*, $OH{\cdot}CH(CO{\cdot}NHMe)_2$, has m. p. 153—154°. Methyl mesoxalate and ethyl mesoxalate can be prepared with almost quantitative yields by the action of bromine on the corresponding tartronates (compare Conrad and Brückner, Abstr., 1892, i, 40). When an alcoholic solution of ethyl mesoxalate is treated with an alcoholic solution of ammonia, a *substance* is precipitated which readily loses ammonia, and is not the expected amide. If the substance is treated with a dilute methyl-alcoholic solution of hydrochloric acid, ammonium chloride is precipitated, and the solution on evaporation yields mesoxalamide. The amide can be obtained pure only in this way (compare Petriew, Abstr., 1878, 490). Jaeger.—The large, colourless, transparent crystals are rhombic-pyramidal: $a:b=0{\cdot}8947:1$ ($b:c$ could not be determined). Ethyl acetoxymalonate has m. p. 68° (Petriew, *loc. cit.*, gave 145°). R. V. S.

Zinc Formaldehydesulphoxylate. Wilh. Becker (*Ber.*, 1910, 43, 856—857. Compare Bazlen, this vol., i, 40).—The di-zinc salt of formaldehydesulphoxylic acid is readily prepared by saturating a

cold mixture of 80 grams of zinc dust (90%) and 400 grams of water with sulphur dioxide, and then adding the requisite amount of formaldehyde solution. The zinc slime is removed, and the filtrate kept at the ordinary temperature for six to eight days, when crystals of the pure salt, $ZnSO_2,CH_2O,H_2O + 2H_2O$, separate.

When the filtrate is warmed for an hour on the water-bath, the compound $ZnSO_2,CH_2O,H_2O$ is obtained as minute rhombohedra.

J. J. S.

Action of Bases on Chloral Hydrate. J. E. Enklaar (*Rec. trav. chim.*, 1910, [ii], **14**, 173—184. Compare Abstr., 1905, i, 170, 741).—Continuing his study of the above reaction, the author confirms his former statement that it is unimolecular in dilute solutions at 0°. At higher temperatures (15°, 20°, 30°) it is slower than the molecular formula would require, but the constants at these temperatures do not approximate to those of a bimolecular reaction. This behaviour (as also the results of Böttger and Kötz, Abstr., 1902, i, 659, and even of Werner, Trans., 1904, **85**, 1376) is explained by the supposition that a salt of chloral hydrate is formed and undergoes partial hydrolysis, the extent of which will depend largely on the temperature. R. V. S.

Stability of β-Ketonic Aldehydes. François Couturier (*Compt. rend.*, 1910, **150**, 705—706. Compare Abstr., 1905, i, 570).—Condensation of ζ-methylheptan-β-one with ethyl formate in presence of sodium leads to the formation of an unstable *methyloctanal*, which has been isolated in the form of its *copper* derivative, $(C_9H_{16}O_2)_2Cu$, m. p. 112°. ζ-Methylhepten-β-one does not condense with ethyl formate.

iso*Propylideneacetoacetaldehyde*, $CMe_2{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$, is obtained from mesityl oxide. The *copper* salt occurs in black crystals, m. p. 134°; the aldehyde undergoes decomposition when distilled. n-*Butyleneacetoacetaldehyde*, $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$, prepared from allylacetone, forms a blue, crystalline *copper* salt, m. p. 136°; the free aldehyde has b. p. 58°/13 mm. with slight decomposition.

The stability of β-ketonic aldehydes diminishes as the ethylenic linking approaches the ketonic group. W. O. W.

Chemical Action of Light. XVI. Giacomo Ciamician and Paul Silber (*Ber.*, 1910, **43**, 945—949; *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 364—367).—A mixture of acetone and methyl alcohol, in the proportion 1 : 2, is exposed to light for a very long time, and is then distilled on the water-bath and, finally, with steam; the residue is found to consist of *iso*butylene glycol. Acetone and ethyl alcohol, after exposure to light during the summer and autumn months, leave, after the removal of the portions volatile with steam, a liquid which, despite its constant b. p., 177°, is certainly a mixture, one constituent of which is *iso*amylene βγ-glycol, since treatment with hot dilute sulphuric acid results in the formation of methyl *iso*propyl ketone (semicarbazone, m. p. 112°).

The prolonged action of light on a mixture of acetone and benzyl alcohol results, not in the formation of an additive compound as in the two preceding cases, but in the oxidation of the alcohol, dihydrobenzoin and *iso*dihydrobenzoin being produced. C. S.

Alkylation of Aliphatic Ketones by the Use of Sodamide. Fission of Hexa-alkylacetones. Albin Haller and Edmond Bauer (*Compt. rend.*, 1910, **150**, 661—667. Compare Abstr., 1904, i, 600).—When aliphatic ketones are alkylated by the method already described, the ultimate product is a hexa-alkylacetone of the type CRR′R″·CO·CRR′R″. When such a compound is boiled with sodamide in presence of an aromatic hydrocarbon, decomposition occurs, with production of an aliphatic hydrocarbon and a trialkylacetamide, unless the ketone is unsymmetrical, when two hydrocarbons and two amides are obtained (compare Abstr., 1909, i, 131, 654).

When methyl iodide is boiled in ethereal solution with the product of the action of diethyl ketone on sodamide, the mixture contains ethyl *iso*propyl ketone, di*iso*propyl ketone, and a *compound*, $C_{15}H_{26}O$, b. p. 148—152°/18 mm. The action of ethyl iodide on the sodium derivative of di*iso*propyl ketone leads to the formation of *ββδ-trimethylhexan-γ-one*, $CHMe_2·CO·CMe_2Et$, b. p. 158—161°; on reduction this yields *ββδ-trimethylhexan-γ-ol*, $C_9H_{20}O$, b. p. 170—171°; the *phenylurethane* has m. p. 164°. *γγεε-Tetramethylheptan-δ-one*,

$$CMe_2Et·CO·CMe_2Et,$$

prepared in the same way, has b. p. 196—198°; *γγεε-tetramethylheptan-δ-ol*, $C_{11}H_{24}O$, has b. p. 210—212°, and forms a *phenylurethane*, m. p. 62—63°.

When *ββδδ*-tetramethylpentan-*γ*-one is boiled with benzene and sodamide, *β*-methylpropane is formed, together with *ββ*-dimethylpropionamide. Under the same conditions, the unsymmetrical compound, *ββδδ*-tetramethylhexan-*γ*-one, yields the same substances, and also *β*-methylbutane and *αα*-dimethylbutyramide. The reaction follows a parallel course with *γγεε*-tetramethylheptan-δ-one and *ββδδ*-tetramethylhexan-*γ*-one (compare this vol., i, 219). W. O. W.

Isolation of a Biose Derived from Amygdalin. Jean Giaja (*Compt. rend.*, 1910, **150**, 793—796. Compare Auld, Trans., 1908, **93**, 1251—1276; Armstrong, Abstr., 1908, i, 741).—At the commencement of the hydrolysis of amygdalin by the digestive juice of *Helix pomatia*, the reducing power of the sugar produced is one-quarter to one-third of that required by the hypothesis that a reducing disaccharide is formed. The reducing properties of the solution are entirely due to dextrose, but a biose is formed as an intermediate product, and has now been isolated. The substance has been obtained as an amorphous powder, insoluble in alcohol, but very soluble in water; it does not undergo fermentation by yeast, but is readily hydrolysed by the juice of snails, dextrose being the only product. The suggestion is put forward that the compound has a constitution resembling that of trehalose. W. O. W.

Influence of Salts on the Optical Rotatory Power of Sucrose and Raffinose. Edward W. Washburn (*Zeitsch. Ver. deut. Zuckerind*, 1910, 381—385).—The measurements were made with a high degree of accuracy, using specially purified materials. Sodium chloride slightly diminishes the rotatory power of sucrose

according to the formula: $[\alpha]_D^{25} = 66{\cdot}41° - 1{\cdot}456R$, where R is the ratio of the amount of salt to that of sucrose present.

The rotatory power of raffinose is very slightly increased by sodium, potassium, or lithium chlorides. The influence of lithium chloride, tested at three different concentrations, is linear. E. F. A.

Coagulation of Starchy Material by Freezing. Giovanni Malfitano and Mlle. A. Moschkoff (*Compt. rend.*, 1910, 150, 710—711).—When a 2% solution of potato starch is cooled, a coagulum separates, whilst the residual liquid retains most of the mineral matter, together with some starch. If the coagulum is washed and the operation repeated, the liquid is found to contain only traces of starch and mineral matter. The process affords, therefore, a convenient method for purifying starchy materials. The quantity of starch remaining in the residual liquid appears to depend on the amount of electrolytes present.

The author considers that his experiments support the view put forward (Abstr., 1906, i, 804) to explain the condition of starch molecules in colloidal solutions. W. O. W.

Hydrolysis of Cellulose with Hydrofluoric Acid. Jules Ville and W. Mestrezat (*Compt. rend.*, 1910, 150, 783—784).—Dilute hydrofluoric acid (5—30%) has little effect on cellulose. More concentrated acid brings about destructive hydrolysis. By heating on the water-bath with the 50% acid for six hours, a 50% yield of dextrose is obtained. W. O. W.

Degradation of Cotton Cellulose. Carl G. Schwalbe and W. Schulz (*Ber.*, 1910, 43, 913—917).—Guignet's soluble cellulose (Abstr., 1889, 847) is exceedingly resistant to hydrolysis. When boiled with dilute sulphuric acid, the reducing power decreases, indicating reversion. It is stable at 105°, dissolves to the extent of 70% in 10% alkali hydroxide, and only gives a coloration with iodine solution on the addition of sulphuric acid. More concentrated sulphuric acid converts it into a substance showing a higher reducing power than "parchment," and differing also from the latter in resisting hydrolysis. Flechsig's amyloid is also different from "parchment"; it is completely soluble in 10% alkali hydroxide, decomposes at 105°, and only shows a coloration with iodine in presence of sulphuric acid. Ekström's acid cellulose is characterised by the great increase in the reducing power on hydrolysis, and the coloration with iodine in the absence of sulphuric acid.

By the action of 69% sulphuric acid on cellulose, 20% of dextrose was obtained, partly crystalline, partly as phenylosazone. To obtain satisfactory yields, the acid should be neutralised with barium carbonate and not with sodium hydroxide. By Ekström's process 44% of dextrose was obtained. The largest amount of dextrose was obtained in experiments showing only very small reducing power. The reducing power was much increased, however, when barium carbonate was substituted for sodium hydroxide to neutralise the acid.

A mixture of dextrose and Guignet's soluble cellulose shows a lower reducing power than the sum of the reducing powers of the components. In hydrolysis when the reducing power is high, possibly the crystallisation of the dextrose is hindered by the by-products, or these by-products (dextrins) have themselves a high reducing power, and this reduction is an indication of incomplete hydrolysis. On the other hand, when the reducing power of the hydrolysed mixture is low, the true reducing power of the sugar present is to some extent masked by the formation of loose compounds with the by-products. These are destroyed by neutralisation and evaporation, as the dextrose can then be caused to crystallise. E. F. A.

Behaviour of Cellose towards Certain Enzymes. Emil Fischer and Géza Zemplén (*Annalen*, 1910, **372**, 254—256. Compare Abstr., 1909, i, 209).—The authors confirm the observation of Bertrand and Holderer (compare this vol., i, 212) that cellose is hydrolysed by the enzymes of *Aspergillus niger*. It is also found that cellose is hydrolysed slowly by an extract of Kephir. W. H. G.

Crystallographic Properties of Some Compounds of Ethylenediamine. Max Frank (*Zeitsch. Kryst. Min.*, 1910, **47**, 346—362). —The following compounds have been examined crystallographically: Diethylenediaminecopper chloride, $Cu[en_2]_2Cl_2,2H_2O$, monoclinic [$a:b:c=0{\cdot}3917:1:0{\cdot}82724$; β 110°30′], and the bromide,

$$Cu[en_2]_2Br_2,2H_2O,$$

monoclinic [$a:b:c=0{\cdot}41831:1:0{\cdot}83415$; β 111°45′]. Triethylenediaminenickel chloride, $Ni[en_2]_3Cl_2,2H_2O$, rhombic [$a:b:c=0{\cdot}68598:1:1{\cdot}0557$], and the bromide, $Ni[en_2]_3Br_2,2H_2O$, rhombic [$a:b:c=0{\cdot}7299:1:1{\cdot}0604$]. The members of each of the preceding pairs are isomorphous, as also are the following: Triethylenediaminezinc chloride, $Zn[en_2]_3Cl_2$, rhombic [$a:b:c=0{\cdot}6236:1:0{\cdot}9482$], the bromide, $Zn[en_2]_3Br_2$, rhombic [$a:b:c=0{\cdot}74946:1:1{\cdot}21430$], and the iodide,

$$Zn[en_2]_3I_2,$$

rhombic [$a:b:c=0{\cdot}53282:1:0{\cdot}8977$]. Triethylenediaminecadmium bromide, $Cd[en_2]_3Br_2$, rhombic [$a:b:c=0{\cdot}69718:1:1{\cdot}1014$], and the iodide, $Cd[en_2]_3I_2$, rhombic [$a:b:c=0{\cdot}7864:1:1{\cdot}0212$]. Triethylenediaminecadmium sulphate, $Cd[en_2]_3SO_4$, rhombic [$a:b:c=0{\cdot}57735:1:x$], and the zinc salt, $Zn[en_2]_3SO_4$. The following are also described: Diethylenediaminecopper nitrate, $Cu[en_2]_2(NO_3)_2,2H_2O$, monoclinic [$a:b:c=1{\cdot}3034:1:0{\cdot}7997$; β 110°49′]. Triethylenediaminecopper thiocyanate, $Cu[en_2]_3(SCN)_2,5H_2O$, rhombic

[$a:b:c=0{\cdot}46807:1:0{\cdot}65231$].

Ethylenediaminecopper acetate, $Cu[en_2](C_2H_3O_2)_2,H_2O$, monoclinic [$a:b:c=0{\cdot}9556:1:1{\cdot}3396$; β 107°49′]. Triethylenediaminenickel iodide, $Ni[en_2]_3I_2,H_2O$, rhombic [$a:b:c=0{\cdot}9195:1:0{\cdot}5486$]. Triethylenediaminenickel thiocyanate, $Ni[en_2]_3(SCN)_2$, monoclinic [$a:b:c=1{\cdot}071:1:0{\cdot}6087$; β 95°32′]. Diethylenediaminenickel cyanide, $Ni[en_2]_2(CN)_2$, rhombic [$a:b:c=0{\cdot}78036:1:0{\cdot}5840$]. Triethylenediaminezinc thiocyanate, $Zn[en_2]_3(SCN)_2$, monoclinic [$a:b:c=0{\cdot}9992:1:0{\cdot}6749$; β 103°16′]. Diethylenediaminecadmium thio-

cyanate, $Cd[en_2]_2(SCN)_2$, monoclinic [$a:b:c = 1{\cdot}1469:1:1{\cdot}1145$; β 109°45′]. Ethylenediammoniumzinc thiocyanate,

$$Zn[C_2H_4N_2H_6](SCN)_4,4H_2O,$$

monoclinic [$a:b:c = 2{\cdot}023:1:0{\cdot}9497$; β 100°7′]; the cadmium salt, $Cd[C_2H_4N_2H_6](SCN)_4$, monoclinic [$a:b:c = 1{\cdot}0313:1:1{\cdot}0628$; β 108°36′]. Ethylenediammoniumzinc sulphate, $Zn[C_2H_4N_2H_6](SO_4)_2,6H_2O$, monoclinic [$a:b:c = 0{\cdot}74897:1:0{\cdot}49606$; β 107°22′]. C. S.

Preparation of β-Methyltetramethylenediamine. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 216808).—The conversion of β-methyladipodiamide,

$$NH_2{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2,$$

into αδ-diamino*iso*pentane, $NH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, has previously been accomplished, but it is now found that the reaction will take place in aqueous solution.

A cooled solution of bromine in sodium hydroxide is treated with the requisite quantity of the diamide, and the mixture warmed at 60—70°, the isolation of the required base being subsequently effected by known methods. F. M. G. M.

White Precipitate. M. Zipkin (*Chem. Zentr.*, 1909, ii, 1914—1915; from *Apoth. Zeit.*, 1909, **24**, 661—662).—On acting with ethyl iodide on infusible white precipitate, NH_2HgCl, for four months, *tetraethylammonium mercuri-iodide*, $2NEt_4I,3HgI_2$, is obtained as yellow crystals, m. p. 158°. On heating the components on the water-bath for six hours, either alone or in the presence of alcohol, the main product consists of ammonium mercuri-iodide, NH_2I,HgI_2, admixed with small quantities of the corresponding ethylamine compound and a little ammonium chloride. On heating the fusible compound,

$$Hg(NH_3)_2Cl_2,$$

for six hours with methyl iodide, with or without addition of methyl alcohol, *tetramethylammonium mercuri-iodide*, NMe_4I,HgI_2, is obtained, which crystallises from boiling methyl alcohol in yellow leaflets, m. p. 241—242°. The mother liquor yields a considerable quantity of pale yellow needles, which in composition and properties resemble the product obtained previously from the infusible precipitate. On heating oxydimercuriammonium chloride, NH_2HgCl,HgO, for eight hours with methyl iodide on the water-bath and boiling with methyl alcohol, lemon-yellow, leaf-like crystals, m. p. 187—188°, are obtained, which behave like tetramethylammonium mercuri-iodide.

Sodium thiosulphate at the ordinary temperature expels the nitrogen from the two white precipitates, and also from the oxy-compound, almost completely as ammonia; the ammonia-free solution has a strongly alkaline reaction, and probably contains a complex of mercuric and sodium thiosulphates.

The author thinks the following formulæ are more appropriate than the accepted ones. Infusible precipitate, NHg_2Cl,NH_4Cl; fusible precipitate, $NHg_2Cl,3NH_4Cl$, and the oxy-compound, NHg_2Cl,H_2O.

L. de K.

Natural Occurrence of *d*-Asparagine. Hans Pringsheim (*Zeitsch. physiol. Chem.*, 1910, **65**, 89—95).—The naturally-occurring

α-amino-acids are all optically active; hitherto, only one of the two isomeric forms has been found in each case. A seeming exception to this is afforded by *d*-asparagine, isolated by Piutti (*Gazzetta*, 1887, 17, 182) in small quantity, together with a large proportion of *l*-asparagine, from a very considerable quantity of vetch seedlings. Doubt is cast, however, on this observation by the fact that asparagine is relatively easily racemised on boiling with water; the relative greater solubility of *d*-asparagine makes it easy to separate this isomeride. Probably the *d*-asparagine described by Piutti was formed from *l*-asparagine and does not occur naturally. E. F. A.

Compounds of Amino-acids and Ammonia. IV. Peter Bergell and Hanns von Wülfing (*Zeitsch. physiol. Chem.*, 1910, 64, 348—366. Compare Fischer and Königs, Abstr., 1905, i, 31; Königs and Mylo, *ibid.*, 1909, i, 87).—Attempts have been made to prepare the amides of amino-acids by the action of ammonia on the chlorinated acyl-amides. A fairly good yield of glycinamide hydrochloride (m. p. 186—189°) is obtained by the action of aqueous ammonia on chloroacetamide at 0° and subsequent precipitation with alcohol. *dl*-Alaninamide hydrobromide can be obtained directly by vigorously stirring ethyl bromopropionate with 25% aqueous ammonia at 6° and evaporation under reduced pressure at 45°. It crystallises from absolute alcohol, has m. p. 176—177° (corr.), and yields a naphthalenesulphonyl derivative, m. p. 218°.

A good yield of *dl*-aminobutyramide hydrobromide is obtained by shaking ethyl α-bromobutyrate with 25% aqueous ammonia at 0° and evaporating the resulting solution under reduced pressure. It has m. p. 185—188° (corr.). The amide of α-bromo*iso*valeric acid does not react to an appreciable extent with ammonia, even when heated for three hours at 100°.

Bromoisohexoamide, $CHMe_2 \cdot CH_2 \cdot CHBr \cdot CO \cdot NH_2$, obtained by pouring the bromide into aqueous ammonia at 0°, crystallises in slender needles, m. p. 95—97° (corr.), and when heated with alcoholic ammonia at 100° for five hours yields leucinamide hydrobromide (68% yield), which forms long, hard prisms, m. p. 205° (corr.).

Naphthalenesulphonylglycinamide, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH_2 \cdot CO \cdot NH_2$, has m. p. 176—178° (corr.); benzoylglycinamide has m. p. 183—185° (corr.), and *chloroacetylglycinamide*, $CH_2Cl \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH_2$, obtained by the action of an ethereal solution of chloroacetyl chloride on free glycinamide, crystallises in pointed plates, m. p. 130—132° (corr.).

Leucinamide is hydrolysed by trypsin, the *l*-compound being decomposed more readily than the *d*-isomeride. Glycinamide and alaninamide are not hydrolysed by trypsin, and natural asparagine is not decomposed by pancreatin. J. J. S.

Synthesis of Polypeptides. Derivatives of *iso*Leucine. II. Emil Abderhalden and Josef Schuler (*Ber.*, 1910, 43, 907—913. Compare Abstr., 1909, i, 769).—The preparation of *glycyl*-l-iso*leucine*, l-*leucyl*-l-iso*leucine*, and l-*leucyl-glycyl*-d-iso*leucine* is described. Glycyl-l-*iso*leucine is not hydrolysed by pressed yeast juice; it behaves in this

respect similarly to other polypeptides containing the antipodes of the natural amino-acids.

Chloroacetyl-l-iso*leucine*, $CH_2Cl\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt$, softens at 74°, m. p. 81°, $[\alpha]_D^{20}$ −22·03° (±0·2°). *Glycyl*-l-iso*leucine*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt$, crystallises in long, rectangular prisms with constricted ends, which sinter at 245° (corr.), m. p. 257° (corr.) to a brown liquid. Glycyl-*d*-*iso*leucine (compare Abstr., 1909, i, 770) is now found to sinter at 246° (corr.), m. p. 256° (corr.). Glycyl-*l*-*iso*leucine has $[\alpha]_D^{20}$ +13·14°, the *d*-isomeride having $[\alpha]_D^{20}$ −14·7°.

Glycyl-l-iso*leucine anhydride*, $CH_2<\begin{matrix}NH\cdot CO\\CO\cdot NH\end{matrix}>CH\cdot CHMeEt$, closely resembles the antipode, crystallising in spherical aggregates of needles, m. p. 262° (corr., decomp.), $[\alpha]_D^{20}$ −17·48° (±0·3°). *d*-α-*Bromo*iso*hexoyl*-l-iso*leucine*, $CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt$, crystallises in colourless, microscopic octahedra, which sinter at 104° (corr.), m. p. 113° (corr.), $[\alpha]_D^{20}$ +18·95° (±0·6°).

l-*Leucyl*-l-iso*leucine*, prepared by the action of 25% aqueous ammonia on the bromo-compound, crystallises with $1\frac{1}{2}H_2O$ in well-formed, long needles and plates. It sinters at 278° (corr.), m. p. 283·5° (corr.), $[\alpha]_D^{20}$ +53·11° (±0·3°).

d-α-*Bromo*iso*hexoyl*-*glycyl*-d-iso*leucine*, prepared from glycyl-*d*-*iso*leucine, *d*-α-bromo-*d*-*iso*hexoyl chloride, and sodium hydroxide, crystallises in well-formed plates, which sinter at 138°, m. p. 147°, $[\alpha]_D^{20}$ +37·3° (±0·5°).

l-*Leucylglycyl*-d-iso*leucine*, $CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt$, is amorphous; it becomes brown on heating at 215°, sinters at 226° (corr.), m. p. 229—230° (corr., decomp.), $[\alpha]_D^{20}$ +14·97° (±0·2°). It shows a marked biuret reaction. E. F. A.

ε-Amino-α-guanidinohexoic Acid. Emil Fischer and Géza Zemplén (*Ber.*, 1910, 43, 934—936).—ε-Benzoylamino-α-bromohexoic acid reacts with a concentrated aqueous solution of guanidine, forming *ε-benzoylamino-α-guanidinohexoic acid*, $C_6H_5\cdot CO\cdot NH\cdot[CH_2]_4\cdot CH(CO_2H)\cdot NH\cdot C(:NH)\cdot NH_2$, crystallising in colourless needles, m. p. 236—241° (corr., decomp.). On boiling this with hydrochloric acid, the benzoyl group is eliminated and a *hydrochloride*, $C_7H_{14}ON_4,2HCl$, is formed; this is regarded as *ε-amino-α-guanidinohexoic anhydride dihydrochloride*,

$$HCl,NH_2\cdot[CH_2]_4\cdot CH<\begin{matrix}CO-NH,HCl\\NH\cdot C:NH\end{matrix}.$$

It crystallises in microscopic prisms, m. p. 212° (corr.). The *picrate* forms microscopic, yellow crystals, mostly obliquely cut, prisms or plates, m. p. 225—230° (corr., decomp.). The corresponding base has not yet been isolated, and is still under investigation.

α-Bromo-δ-nitrobenzoylaminovaleric acid reacts in the same manner with guanidine. E. F. A.

Aliphatic Nitro-compounds. VII. Influence of Negative Atoms and Groups in Derivatives of Acetonitrile and Acetamide. Wilhelm Steinkopf [with Ludwig Bohrmann,

H. Grünupf, G. Kirchhoff, Boris Jürgens, and C. Benedek] (*J. pr. chem.*, 1910, [ii], 81, 97—149, 193—253).—After pointing out the importance of nitroacetonitrile in connexion with the constitution of fulminic acid, the author details the history of many investigators' unsuccessful attempts to synthesise the nitrile. The author hoped that the reaction between dichloroacetonitrile and hydroxylamine would yield oximinoacetonitrile, which could then be oxidised to nitroacetonitrile. The reaction results, however, in the formation of *dichloroethenylamidoxime*, $CHCl_2 \cdot C(NH_2):NOH$, m. p. 103—104° (decomp.) [*hydrochloride*, m. p. 135° (decomp.); *acetyl* derivative, m. p. 114—115°], and with an excess of hydroxylamine at 60° in the production of *oximinoethenylamidoxime*,

$$NOH:CH \cdot C(NH_2):NOH,$$

m. p. 148—152° (decomp.), the *diacetyl* derivative of which has m. p. 142—150°. In a similar way, by the interaction of the nitrile, hydroxylamine hydrochloride, and sodium carbonate in aqueous solution, a whole series of α-halogenated amidoximes can be prepared, which yield hydrochlorides with hydrogen chloride, acetyl derivatives with cold acetic anhydride, characteristic colour reactions with ferric chloride, and coloured precipitates with copper salts. *Chloroethenylamidoxime*, $CH_2Cl \cdot C(NH_2):NOH$, m. p. 91—92° (decomp.) [*hydrochloride*, m. p. 116—118° (decomp.)], *trichloroethenylamidoxime*, $CCl_3 \cdot C(NH_2):NOH$, m. p. 128—129° (decomp.) [*hydrochloride*, m. p. 140° (decomp.)], *chloro-oximinoethenylamidoxime*, $NOH:CCl \cdot O(NH_2):NOH$, decomposing at 109°, *bromoethenylamidoxime*, $CH_2Br \cdot C(NH_2):NOH$, m. p. 95—96°, *dibromoethenylamidoxime*, $CHBr_2 \cdot C(NH_2):NOH$, m. p. 120° [*hydrochloride*, m. p. 163—165° (decomp.)], *tribromoethenylamidoxime*, $CBr_3 \cdot C(NH_2):NOH$, m. p. 126°, and *iodoethenylamidoxime*, $CH_2I \cdot C(NH_2):NOH$, m. p. 123—124° (decomp.) (*acetyl* derivative, m. p. 103—105°), have thus been obtained. They are all characterised by their stability towards boiling water, hydroxylamine being produced only by heating with water under pressure. *Trichloroacetimino-methyl ether*, $CCl_3 \cdot C(:NH) \cdot OMe$, b. p. 148—149°, obtained by boiling a methyl-alcoholic solution of trichloroacetonitrile, is the first recorded instance of the formation of an imino-ether without the presence of hydrogen chloride; by heating it with aniline on the water-bath, *trichloroacetophenylamidine*, $CCl_3 \cdot C(:NH) \cdot NHPh$, m. p. 101°, is obtained, the *hydrochloride* of which has m. p. 183°.

The author's next attempt to prepare nitroacetonitrile has been more successful. According to Meister, methazonic acid is very probably β-nitroacetaldoxime, the presence of the C·C linking being indicated by the author's discovery that the interaction of methazonic acid and aqueous potassium hydroxide is a very good method of obtaining potassium nitroacetate. If the aldoxime has the *syn*-configuration, dehydration should result in the formation of nitroacetonitrile. This is the case, the nitroacetonitrile obtained by the slow addition of thionyl chloride to a boiling ethereal solution of methazonic acid being purified through the red *ammonium* salt, which decomposes at 130—135°. The presence of the primary nitro-group is proved by Konowaloff's colour reaction with ferric chloride, by the formation of *cyanomethylnitrolic acid*, $CN \cdot C(NO_2):NOH$, with nitrous acid, and by the

formation from ammonium *aci*-nitroacetonitrile and benzenediazonium nitrate of *nitrocyanoformaldehydephenylhydrazone*, $CN\cdot C(NO_2):N\cdot NHPh$, decomposing at 108°, which dyes wool intensely yellow. The presence of the cyano-group is shown by the formation of *nitroethenylamidoxime*, $NO_2\cdot CH_2\cdot C(NH_2):NOH$, decomposing at 108°, from concentrated aqueous hydroxylamine hydrochloride and ammonium *aci*-nitroacetonitrile. Nitroacetonitrile cannot be directly hydrolysed to nitroacetamide, which is produced, however, by passing hydrogen chloride into an ethereal solution of the nitrile and methyl alcohol in a freezing mixture, probably by the decomposition of the initially formed $NO_2\cdot CH_2\cdot C(OMe):NH,HCl$. Concentrated aqueous ammonium *aci*-nitroacetonitrile yields *dichloronitroacetonitrile*, $NO_2\cdot CCl_2\cdot CN$, b. p. 39°/21 mm., and *dibromonitroacetonitrile*, b. p. 57—58°/12 mm., with chlorine and bromine respectively. An ethereal solution of nitroacetonitrile at 0° reacts with amines to form the *amidines*: $C_8H_9O_2N_3$, m. p. 80°, from aniline; $C_9H_{11}O_2N_3$, m. p. 77—78°, from *o*-toluidine; $C_{10}H_{13}O_2N_3$, m. p. 86—86·5°, from *m*-xylidine.

Dipotassium nitroacetate, $CO_2K\cdot CH:NO\cdot OK$, is also produced by boiling concentrated aqueous potassium hydroxide with ammonium fulminate, ammonium *aci*-nitroacetonitrile, ammonium *aci*-nitroacetamide, or nitromethane; it forms colourless crystals, yields nitromethane with dilute sulphuric acid, and nitroacetic acid by treating its suspension in dry ether with hydrogen chloride.

β-Oximino-oxalimino-chloride, $NOH:C(OH)\cdot CCl:NH$, m. p. 157—158°, is obtained by the slow addition of ammonium nitroacetamide to an excess of thionyl chloride, and heating at 50—60°; by the addition of thionyl chloride to ethereal methazonic acid, best in sunlight; and by passing hydrogen chloride into an ethereal suspension of nitroacetamide at 0°, or into an ethereal solution of nitroacetonitrile. The *acetyl* derivative, $OH\cdot C(:NOAc)\cdot CCl:NH$, has m. p. 131°; the *benzoyl* derivative has m. p. 169°; *β-oximino-oxalphenylamidine*, $NOH:C(OH)\cdot C(:NH)\cdot NHPh$, m. p. 185°, is obtained by boiling an aqueous solution of the imido-chloride with aniline, and *β-oximinohydroxamic acid*, $NOH:C(OH)\cdot CO\cdot NH_2$, m. p. 137°, by boiling the concentrated aqueous solution alone. *α-Oximino-oxalimino-chloride*, $NOH:C(OH)\cdot CCl:NH$, m. p. 173—174° (decomp.), obtained by saturating a boiling ethereal solution of methazonic acid with hydrogen chloride, forms an *acetyl* derivative, m. p. 165°, and a *phenylamidine*, $NOH:C(OH)\cdot C(:NH)\cdot NHPh$, m. p. 136—137°. From methazonic acid two *substances*, $C_4H_4O_4N_4$, have been obtained, the constitutions of which have not yet been ascertained; they are called α- and β-methazonic anhydrides. *α-Methazonic anhydride*, m. p. 168°, is produced by the addition of dry methazonic acid to concentrated sulphuric acid at 30—40°. It is easily soluble in dilute alkalis and in ammonium hydroxide; the yellow *sodium* and the white *silver* derivatives of the anhydride are described. The *dibenzoyl* derivative has m. p. 184—185°. An aqueous solution of the sodium derivative and diazobenzene chloride yield the *phenylhydrazone*,

$$C_4H_2O_4N_4,N_2HPh,$$

of the anhydride. By boiling a concentrated aqueous solution of α-methazonic anhydride with aniline hydrochloride, a *substance*,

$C_4H_3O_3N_4Ph$, m. p. 122°, is obtained, which forms yellow crystals; analogous coloured *substances* are obtained from the hydrochlorides of *o*- and *p*-toluidine, *p*- and *m*-phenylenediamine, and anthranilic acid, which decompose at 178—179°, 141°, 220°, 216°, and 226° respectively. *β-Methazonic anhydride*, m. p. 121—122°, is prepared by boiling the α-anhydride with water for seven minutes, recrystallising rapidly from water, and finally precipitating the solution in dilute sodium hydroxide with dilute hydrochloric acid. When the α-anhydride is boiled with water, an *oil*, $C_3H_3O_3N_3$, is formed, which yields a *phenylhydrazone*, m. p. 131°, identical with that obtained from an ammoniacal solution of β-methazonic anhydride and benzenediazonium chloride.

The following substances are obtained by heating equal molecular quantities of a halogenated acetamide and phosphorus pentachloride and exposing the initial, usually oily, product to moist air; *dichloroacetamidophosphoryl dichloride*, $CHCl_2{\cdot}CO{\cdot}NH{\cdot}POCl_2$, m. p. 112—113°, *diethyl* ester, $CHCl_2{\cdot}CO{\cdot}NH{\cdot}PO(OEt)_2$, m. p. 72—73°, *dianilide*, m. p. 219—220°, *bisphenylhydrazide*, m. p. 190° (decomp.); *trichloroacetamidophosphoryl dichloride*, m. p. 146—148°, *dimethyl* ester, m. p. 105—107°, *diethyl* ester, m. p. 47—48°, *dianilide*, m. p. 194—195°, *bisphenylhydrazide*, m. p. 237—238° (decomp.); *tribromoacetamidophosphoryl dichloride*, m. p. 105—106°, which with alcoholic sodium ethoxide gives *diethyl dibromoethoxyacetamidophosphate*, m. p. 91°; the corresponding *methyl* compound has m. p. 92—93°; *diethyl chlorobromoacetamidophosphate* has m. p. 67—68; *dichlorobromoacetamidophosphoryl dichloride*, m. p. 147°, *dimethyl* ester, m. p. 107°, *diethyl* ester, m. p. 76—77°; *dichloronitroacetamidophosphoryl dichloride*, m. p. 165° (decomp.), *diethyl* ester, m. p. 56°; *dibromonitroacetamidophosphoryl dichloride*, m. p. 187—188° (decomp.); *chlorodiphenylacetamidophosphoryl dichloride*, m. p. 122—123°, *dimethyl* ester, m. p. 104—106°; *α-dichloropropionamidophosphoryl dichloride*, $CCl_2Me{\cdot}CO{\cdot}NH{\cdot}POCl_2$, m. p. 127—128°.

The results of the preceding experiments show that negative atoms or groups may exert an inhibiting or a furthering influence on other portions of the molecule of an organic compound. The furthering influence is illustrated by the formation of dichloro- and dibromonitroacetonitrile from nitroacetonitrile, whilst nitromethane yields only bromonitromethane, also by the increased ability of the nitrile group to form additive compounds, not only in nitroacetonitrile, but also in the halogenated nitriles, as, for example, in the unique formation of trichloroacetimido-methyl ether. The inhibiting influence of the negative atoms or groups is shown in the difficulty of hydrolysing nitrophenylacetonitrile or nitroacetonitrile, and the stability of the nitrated and halogenated amidoximes, and especially of β-oximinooxalimido-chloride, towards water. At present there is insufficient evidence for the formulation of general rules regarding the inhibiting and the furthering influence of negative atoms or groups. C. S.

Origin of the Introduction of Magnesium into Organic Syntheses. Philippe Barbier (*Bull. Soc. chim.*, 1910, [iv], 7, 206—208).—The use of magnesium in organic syntheses is not entirely due to Grignard, since it was first employed by the author in the

preparation of dimethylheptenol by the Saytzeff reaction (Abstr., 1899, i, 323). W. O. W.

Pyrogenetic Decomposition of Naphtha in Presence of a Catalyst. Iwan von Ostromisslensky and I. Burschanadze (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 195—207).—The authors regard the formation of aromatic hydrocarbons from naphtha at high temperatures as taking place in two stages, the first being the formation of acetylene and its homologues, and the second being expressed by the reversible equation: $3C_2H_2 \rightleftharpoons C_6H_6$. It is, indeed, found that the proportion of benzene formed from naphtha is considerably increased by the presence of those contact substances, for instance, iron gauze, which facilitate the polymerisation of acetylene into benzene and polycyclic hydrocarbons. In presence of reduced nickel or its oxide, neither naphtha nor benzene yields any liquid product, the proportion of coke formed being largely increased.

Under the influence of iron or ferric oxide, asbestos, pumice, etc., at 600—750°, the hydrocarbons of the aliphatic or aromatic series or mixtures of them, such as naphtha or coal gas, are decomposed to a very considerable extent into carbon and hydrogen. The gas thus obtained may be used for filling balloons, or for heating or lighting purposes. T. H. P.

Freezing Mixtures of Isomeric Xylenes, Nitrotoluenes, and Toluidines. Hermann W. Fischer (*Zeitsch. Elektrochem.*, 1910, 16, 161).—Commercial nitrotoluene (38% *p*-, 60% *o*-, and 2% *m*-nitrotoluene) deposits pure *p*-nitrotoluene on cooling; the eutectic point is reached at −18°. A mixture of the toluidines behaves similarly, but no eutectic point could be reached, even at −50°, and it is very difficult to separate the *p*-toluidine from the viscous mother liquor. *o*- and *m*-Toluidines probably solidify to amorphous glasses at very low temperatures. By freezing a mixture of the xylenes in liquid air and allowing the solid to melt slowly under suction, a solid residue melting at +5° (probably nearly pure *p*-xylene) was obtained; *o*-xylene solidified about −25°, and *m*-xylene about −50°.

Apparently the molecules of these isomerides are not sufficiently similar to make them mutually soluble in the solid state. T. E.

Identity of the Solid Distyrene, m. p. 124°, with Stilbene. Emil Erlenmeyer (*Annalen*, 1910, 372, 247—249).—The substance formed by the dry distillation of calcium cinnamate (Engler and Leist, Abstr., 1873, 901) or β-truxillic acid (Liebermann, Abstr., 1889, 1194), and known as solid distyrene, is shown to be stilbene (compare Stobbe and Posnjak, this vol., i, 235).

Ethyl cinnamate decomposes when heated for several hours, yielding stilbene, the formation of which may be explained on the assumption that two molecules of the ester polymerise, yielding ethyl truxillate, which decomposes subsequently, partly into ethyl cinnamate and partly into stilbene and ethyl maleate. W. H. G.

Liquid and Sold Distyrene. Hans Stobbe (*Annalen*, 1910, 372, 249—251. Compare Stobbe and Posnjak, this vol., i, 235).—The author confirms Erlenmeyer's observation (compare preceding abstract). W. H. G.

Aniline Arsenyl Tartrate. Paul Yvon (*Compt. rend.*, 1910, 150, 834—835. Compare this vol., i, 163).—*Aniline arsenyl tartrate*, $C_4H_5O_6(AsO)\cdot C_6H_7N$, prepared by boiling aniline hydrogen tartrate in aqueous solution with arsenious oxide, crystallises in large, hexagonal tablets, isomorphous with the corresponding antimony salt. At 100°, water is lost, with formation of an anilide. The rotatory power of an aqueous solution diminishes considerably with dilution, probably owing to dissociation; a 2% solution shows $[\alpha]_D$ 24·12°, whilst a 10% solution has $[\alpha]_D$ 58·50°. The substance has D 1·808; 100 grams of water at 15° dissolve 41·84 grams of the salt, and 756·00 grams at 100°; at 18°, 100 grams of alcohol (90%) dissolve 2·21 grams. W. O. W.

Amines. II. Syntheses of *p*-Nitrophenylethylamine and 2:4-Dinitrophenylethylamine. Treat B. Johnson and Herbert H. Guest (*Amer. Chem. J.*, 1910, 43, 310—322).—In continuation of the authors' work on the β-amines (Abstr., 1909, i, 784), a study has been made of the nitro-derivatives of phenylethylamine.

Acetophenylethylamide (Bischler and Napieralski, Abstr., 1893, i, 608) can be obtained in a yield of 98% of the theoretical by the action of thioacetic acid on phenylethylamine, and when treated with concentrated nitric acid is converted into a mixture of *o*- and *p*-acetonitrophenylethylamide. The p-*nitro*-compound,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NHAc,$$

m. p. 141—142°, is obtained in a yield of about 70% of the theoretical; it forms colourless, prismatic crystals, and is oxidised by potassium dichromate with production of *p*-nitrobenzoic acid; its *hydrochloride* has m. p. 179—180° (decomp.). The o-*nitro*-compound, m. p. 86—88°, crystallises in slender prisms, and is hydrolysed by hydrobromic acid with formation of o-*nitrophenylethylamine*, which gives a crystalline *picrate*, m. p. 147°.

p-*Aminophenylethylamine*, $NH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2$, is obtained as an oil by reducing aceto-*p*-nitrophenylethylamide with tin and hydrochloric acid; the *hydrochloride* decomposes at 270—280°; the *platinichloride* has not a definite m. p., and the *picrate* has m. p. 223—224° (decomp.). *Aceto*-p-*aminophenylethylamide*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NHAc,$$

obtained by the reduction of the corresponding nitro-derivative with aluminium amalgam, crystallises in radiating prisms, sinters above 170°, and decomposes at 191—192°.

Aceto-2 : 4-*dinitrophenylethylamide*, $C_6H_3(NO_2)_2\cdot CH_2\cdot CH_2\cdot NHAc$, m. p. 97—98°, obtained by the action of a mixture of sulphuric and nitric acids on acetophenylethylamide or its *p*-nitro-derivative, crystallises in prisms, and on oxidation with potassium dichromate yields 2 : 4-dinitrobenzoic acid.

Phthalylphenylethylimide, $CH_2Ph{\cdot}CH_2{\cdot}N{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_4$, m. p. 133°, prepared by heating phenylethylamine with phthalic anhydride, forms well-defined prisms, and, when treated with concentrated nitric acid, is converted into *phthalyl*-2 : 4-*dinitrophenylethylimide*, m. p. 215°, which crystallises in colourless, rhombic prisms.

p-*Nitrophenylethylamine*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, is obtained as a yellow oil by the hydrolysis of aceto-*p*-nitrophenylethylamide with hydrobromic or hydrochloric acid; it is a strong base, and absorbs carbon dioxide from the air to form a crystalline *carbonate*. The *hydrobromide*, m. p. 218—219°, the *hydrochloride*, m. p. 212—214°, and the *platinichloride*, which decomposes at 223°, are described. The amine reacts with phenylthiocarbimide to form *α-phenyl-β*-p-*nitrophenylethylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, m. p. 136°, which crystallises in stout prisms. *Benzenesulphonyl*-p-*nitrophenylethylamide*, $PhSO_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, m. p. 107—108°, crystallises in prisms; the *methyl* derivative, $PhSO_2{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, m. p. 98°, forms rectangular crystals.

2 : 4-*Dinitrophenylethylamine*, $C_6H_3(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, obtained as an oil by the hydrolysis of aceto-2 : 4-dinitrophenylethylamide or the corresponding phthalimide with hydrochloric acid, yields a crystalline *hydrochloride*, m. p. 197—198°, and *picrate*, m. p. 159°. *α-Phenyl-β*-2 : 4-*dinitrophenylethylthiocarbamide*,

$$NHPh{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4(NO_2)_2,$$

m. p. 128°, crystallises in plates. E. G.

Reaction of Imino-chlorides with Salts of Organic Acids and with Potassium Cyanide. Otto Mumm [and, in part, Hugo Hesse] (*Ber.*, 1910, **43**, 886—893).—When a solution of *α*-chlorophenylbenzylideneamine or of *α*-chloro-*p*-nitrophenylbenzylideneamine in ether or petroleum is shaken for twenty-four hours with an aqueous solution of a salt of an organic acid, a reaction occurs which may be represented thus: $NPh{:}CPhCl + CH_3{\cdot}CO_2Na =$

$$NaCl + NPh{:}CPh{\cdot}OAc \longrightarrow NPhAc{\cdot}COPh.$$

In this way formylbenzanilide, acetylbenzanilide, and dibenzoylaniline have been obtained from *α*-chlorophenylbenzylideneamine and sodium formate, acetate and benzoate respectively, whilst sodium glycollate yields *hydroxyacetylbenzanilide*, m. p. 151°, and sodium cinnamate gives *cinnamoylbenzanilide*, m. p. 136°. In a similar way, *formylbenz*-p-*nitroanilide*, m. p. 165°, *acetylbenz*-p-*nitroanilide*, m. p. 180°, and *dibenzoyl*-p-*nitroaniline*, m. p. 203°, are obtained from *α*-chloro-*p*-nitrophenylbenzylideneamine.

The first stage of the preceding reaction also proceeds during the interaction of imino-chlorides and potassium cyanide; thus benzanilide and *α*-chloro-*p*-nitrophenylbenzylideneamine yield phenyliminobenzoyl cyanide (Sachs, Abstr., 1901, i, 272) and *p*-nitrophenyliminobenzoyl cyanide respectively. C. S.

Action of Acetone on Sodium Phenyl Carbonate. J. Moll van Charante and P. J. Montagne (*Chem. Weekblad*, 1910, 7, 166—167. Compare Moll van Charante, Abstr., 1908, i, 175; Franchimont, Abstr., 1909, i, 4).—Franchimont's statement that the

interaction of sodium phenyl carbonate and acetone dried over phosphoric oxide does not yield a vigorous evolution of carbon dioxide is admitted by him to be incorrect. A. J. W.

Preparation of Halogen and Amino-derivatives of Aromatic Ethers. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 216642).—Products obtained by the interaction of diazotised *peri*-aminonaphtholsulphonic acids with aminophenyl ethers have previously been described; the halogen derivatives of these ethers are now found to give satisfactory results, and the following are described in the patent.

p-*Chloro*-o-*aminophenyl ether*, $C_6H_5\cdot O\cdot C_6H_3Cl\cdot NH_2$, m. p. 45°, colourless prisms.

p-*Chloro*-o-*aminophenyl* m-*tolyl ether*, $C_6H_4Me\cdot O\cdot C_6H_3Cl\cdot NH_2$, m. p. 43·5°, b. p. 210°/17 mm.; warm concentrated sulphuric acid yields a *sulphonic acid*.

p-*Chloro*-o-*aminophenyl* p-*tolyl ether*, colourless needles, m. p. 55·5°; the *hydrochloride* is sparingly soluble, and dissociates with water. Concentrated sulphuric acid gives a sparingly soluble *sulphonic acid*.

2-*Chloro*-2′-*aminophenyl ether*, $NH_2\cdot C_6H_4\cdot O\cdot C_6H_4Cl$, yellow oil, decomposes when distilled under atmospheric pressure, b. p. 197°/23 mm.; the *sulphonic acid* is readily soluble in water.

4-*Chloro*-2′-*aminophenyl ether* is a yellow oil, b. p. 208°/26 mm.; the *sulphonic acid* is sparingly soluble in water.

4 : 2′-*Dichloro*-2-*aminophenyl ether*, $NH_2\cdot C_6H_3Cl\cdot O\cdot C_6H_4Cl$, is a viscous oil, b. p. 219°/20 mm.; the *sulphonic acid* is described.

4 : 4′-*Dichloro*-2-*aminophenyl ether*, colourless needles, m. p. 65°, is readily soluble in organic solvents; the *hydrochloride* (long, colourless needles) is sparingly soluble; sulphuric acid (20% anhydride) at 100° yields a *product* of high melting point which is insoluble in water, ammonium hydroxide, or sodium carbonate.

2-*Chloro*-4′-*aminophenyl ether*, $NH_2\cdot C_6H_4\cdot O\cdot C_6H_4Cl$, m. p. 82·5°, is sparingly soluble in alcohol; the sulphonated product is not readily soluble in water.

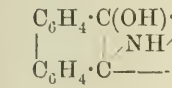
4-*Chloro*-4′-*aminophenyl ether* forms yellow prisms, m. p. 100°; the *hydrochloride* and *sulphonic acid* are described.

2 : 4′-*Dichloro*-4-*aminophenyl ether*, $NH_2\cdot C_6H_3Cl\cdot O\cdot C_6H_4Cl$, has m. p. 74°, and darkens rapidly on exposure to air; the *sulphonic acid* is sparingly soluble; sulphuric acid (20% anhydride) yields a *compound* which is insoluble in water or alkalis.

The preparation and properties of numerous dyes prepared from these compounds combined with diazotised aminonaphtholsulphonic acids are described and tabulated in the patent. F. M. G. M.

Phenanthrene Series. XXVII. Action of Ammonia and Amines on 9-Hydroxyphenanthrene, 9 : 10-Dihydroxyphenanthrene (Hydrophenanthraquinone), and 3-Bromo-9(10)-hydroxyphenanthrene. Julius Schmidt and Hermann Lumpp (*Ber.*, 1910, 43, 787—794).—The reaction between ammonia and 9 : 10-dihydroxyphenanthrene has been studied with the object of obtaining an in-

expensive method for the preparation of the corresponding diamino-derivative; only one of the hydroxy-groups, however, is reactive, and the product is a 9-diphenanthrol-10-amine, $NH(C_{14}H_8{\cdot}OH)_2$, which is not identical with the product obtained by the action of ammonia on 9-chloro-10-hydroxyphenanthrene (Abstr., 1909, i, 35). It is suggested that the latter compound has the normal structure $NH(C_{14}H_8{\cdot}OH)_2$, but that the former compound has the annexed isomeric formula.



(I.)

9 : 10-Dihydroxyphenanthrene is readily prepared by reducing phenanthraquinone with zinc dust and glacial acetic acid. *Di-9-hydroxyphenanthryl-10-amine*, $C_{28}H_{19}O_2N$ (formula I), forms a brown powder, m. p. 385°. Its salts with mineral acids are hydrolysed by water, and its solution in sulphuric acid has a blue colour.

Boiling aniline reacts with 9 : 10-dihydroxyphenanthrene, yielding *9-hydroxy-10-anilinophenanthrene*, $OH{\cdot}C_{14}H_8{\cdot}NHPh$, which crystallises in pale green prisms, m. p. 165°. Its solution in concentrated sulphuric acid has a pale yellow colour, but gives an intense red coloration with a trace of potassium nitrate.

Di-9-phenanthrylamine, $NH(C_{14}H_9)_2$, prepared by heating 9-hydroxyphenanthrene with a concentrated aqueous solution of ammonium hydroxide on the water-bath, forms a pale brown mass, m. p. 370°. Its solution in concentrated sulphuric acid has an intense blue colour, but in the presence of a trace of the original hydroxy-compound the colour changes to green.

Di-3-bromo-9(10)-phenanthrylamine, $NH(C_{14}H_8Br)_2$, obtained from 3-bromo-9(10)-hydroxyphenanthrene and aqueous ammonium hydroxide, forms brown, flocculent masses, and is a feeble base.

3-Bromo-9 : 10-dihydroxyphenanthrene, $C_{14}H_7Br(OH)_2$, obtained by reducing 3-bromophenanthraquinone with zinc dust and glacial acetic acid, forms a colourless, flocculent mass, m. p. 220°. The *acetyl* derivative, $C_{18}H_{13}O_4Br$, forms reddish-brown crystals, m. p. 176—178°.

J. J. S.

Preparation of Aminoacylcatechols. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 216640).—The action of phthalimido-fatty acid chlorides on catechol ethers in the presence of aluminium chloride yields phthalimidoacylcatechol ethers, which, on treatment with acid, are converted into aminoacylcatechols.

Phthalimidoacetoveratrole, $C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH_2{\cdot}CO{\cdot}C_6H_3(OMe)_2$, m. p. 202°, prepared from veratrole and phthalyl glycyl chloride, when heated at 150° during one hour with concentrated hydrochloric acid (15 parts) and glacial acetic acid (20 parts) yields on addition of ammonium hydroxide *aminoacetocatechol*; its *hydrochloride* forms colourless needles, m. p. about 260°; this decomposition may be effected in two stages, the phthalic acid residue being eliminated by boiling under reflux, and the methyl groups subsequently under pressure.

α-Phthalimidopropionylveratrole,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CHMe\cdot CO\cdot C_6H_3(OMe)_2,$$

m. p. 212°, is prepared analogously from α-phthalimidopropionyl chloride, and yields *α-aminopropionylveratrole*, a white, crystalline powder, m. p. 220°, which on further heating forms 4-*α-aminopropionylcatechol*, $NH_2\cdot CHMe\cdot CO\cdot C_6H_3(OH)_2$, a yellow powder, m. p. 212°; its *hydrochloride*, rose-coloured leaflets, m. p. 236°, is soluble in water, and gives a green colour with ferric chloride.

4-*β-Aminopropionylcatechol*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot CH_2\cdot NH_2$, a brownish-grey powder, decomposes without melting when heated; the *hydrochloride*, leaflets, m. p. 240°, gives a characteristic green coloration with ferric chloride. F. M. G. M.

Method of Formation of Dithymol. A. Brissemoret and Blanchetière (*Bull. Soc. chim.*, 1910, [iv], 7, 235—236. Compare Cousin, Abstr., 1908, i, 84, 162).—The presence of a ferment is not necessary for the conversion of thymol into dithymol. This substance can be prepared by dissolving thymol (16 grams) in 300 c.c. of alcohol and 200 c.c. of hydrogen peroxide (12 volumes), and allowing the mixture to remain for three weeks in sunlight. W. O. W.

Condensation of Benzaldehyde with Guaiacol. Wilhelm Manchot (*Ber.*, 1910, 43, 949—951).—The condensation products of aromatic aldehydes and guaiacol or creosol are generally viscous, the only exception being the crystalline substance obtained from benzaldehyde and guaiacol. A cold mixture of concentrated sulphuric acid and glacial acetic acid is added to a solution of guaiacol (2 mols.) and benzaldehyde (1 mol.) in glacial acetic acid cooled below 0°. After five hours the mixture is poured on ice; the red oil after purification is obtained in colourless crystals, m. p. 148°, which are soluble in dilute sodium hydroxide. The analytical data and the molecular weight indicate that the substance is *phenyldiguaiacylmethane*,

$$CHPh[C_6H_3(OH)\cdot OMe]_2.$$

C. S.

p-**Thiocresol.** Theodor Zincke and W. Frohneberg (*Ber.*, 1910, 43, 837—848. Compare Abstr., 1909, i, 643).—Bromine and chlorine react with a glacial acetic acid solution of *p*-thiocresol, yielding the corresponding sulphonyl chloride and bromide, an intermediate product being the disulphide. This reaction appears to be characteristic of the aromatic mercaptans as a class. With carbon tetrachloride solutions at 100°, bromine yields 3 : 3′-di- or 2 : 2′ : 5 : 5′-tetra-substituted derivatives of the disulphide.

When the methyl derivative, $C_6H_4Me\cdot SMe$, reacts with chlorine in carbon tetrachloride solution, the substituted derivative,

$$C_6H_4Me\cdot SCCl_3,$$

is obtained, whereas a solution of bromine yields an additive compound, $C_6H_4Me\cdot SMeBr_2$, or substituted derivatives,

$$C_6H_3BrMe\cdot SMeBr_2$$

and $C_6H_2Br_2Me\cdot SMeBr_2$. The additive products readily exchange the two bromine atoms for oxygen, yielding sulphoxides; they also react with sodium hydrogen sulphite, giving up the two bromine atoms and yielding the sulphides, which can be oxidised by nitric acid or hydrogen peroxide to the sulphoxides or sulphones.

When the methyl derivative is brominated in the absence of a solvent, the methyl group is removed and a dibromo-disulphide is obtained, which, on further bromination in carbon tetrachloride solution, yields the same tetrabromo-derivative as is obtained when the thiocresol is brominated in carbon tetrachloride solution. The dibromo-disulphide obtained from the methyl derivative contains the two bromine atoms in the *o*-positions with respect to the methyl groups, as it yields a sulphonyl chloride identical with that obtained from *o*-bromotoluenesulphonic acid.

p-*Toluenesulphonyl bromide*, $C_6H_4Me\cdot SO_2Br$, crystallises in colourless, flat prisms, m. p. 93—94°.

3 : 3′-*Dibromo*-p-*ditolyl disulphide*, $S_2(C_6H_3BrMe)_2$, crystallises in glistening plates, m. p. 88°, and reacts with chlorine in glacial acetic acid solution, yielding 3-*bromo*-p-*toluenesulphonyl chloride*, $C_6H_3BrMe\cdot SO_2Cl$, m. p. 80°. 2 : 2′-*Dibromo*-p-*ditolyl disulphide* forms stout, colourless needles, m. p. 100°, and yields with chlorine, 2-bromo-*p*-toluene sulphonyl chloride, m. p. 60° (Hayduck, *Annalen*, 1874, 172, 207, gives 54°).

2 : 2′ : 5 : 5′-*Tetrabromo*-p-*ditolyl disulphide*, $S_2(C_6H_2Br_2Me)_2$, crystallises in compact, colourless cubes, m. p. 169—170°.

2-*Bromo*-p-*thiocresol*, $C_6H_3BrMe\cdot SH$, obtained from the corresponding disulphide by reducing with potassium sulphide, forms small crystals, m. p. 40°, and is readily oxidised to the disulphide.

p-*Tolyl methyl sulphide dibromide*, $C_6H_4Me\cdot SMeBr_2$, obtained by the addition of bromine to Auwers and Arndt's *p*-tolyl methyl thioether (Abstr., 1909, i, 175), crystallises in yellowish-red needles, m. p. 55—60° (decomp.). The corresponding *sulphoxide*, $C_6H_4Me\cdot SMeO$, has b. p. 168°/38 mm. and m. p. 50—54°; it is deliquescent, yields a sparingly soluble compound with mercuric chloride, and reacts with fuming hydrobromic acid, yielding the dibromide, $C_6H_4Me\cdot SMeBr_2$.

2-*Bromo*-p-*tolyl methyl sulphide dibromide*, $C_6H_3MeBr\cdot SMeBr_2$, forms long, brownish-red needles, m. p. 90—95° (decomp.). The *sulphoxide*, $C_6H_3MeBr\cdot SMeO$, has b. p. 198—200°/30 mm., and the *sulphone*, $C_6H_3MeBr\cdot SMeO_2$, m. p. 101°.

2 : 5-*Dibromo*-p-*tolyl methyl sulphide dibromide*, $C_6H_2MeBr_2\cdot SMeBr_2$, crystallises in red needles, m. p. 100—105° (decomp.), and the *sulphoxide*, $C_6H_2MeBr_2\cdot SMeO$, forms long, slender needles, m. p. 128°.

2-*Bromo*-p-*tolyl methyl sulphide*, $C_6H_3MeBr\cdot SMe$, is a colourless, odourless oil, b. p. 158°/25 mm., and the corresponding 2 : 5-*dibromo*-derivative, $C_6H_2MeBr_2\cdot SMe$, crystallises in long, colourless needles, m. p. 86°.

p-*Tolyl trichloromethyl sulphide*, $C_6H_4Me\cdot S\cdot CCl_3$, has b. p. 150°/15 mm. and m. p. 23°. It reacts with aniline, yielding *p*-thiocresol and triphenylguanidine. 2-*Bromo*-p-*tolyl trichloromethyl sulphide*, $C_6H_3MeBr\cdot S\cdot CCl_3$,

crystallises in well developed plates, m. p. 57°. A by-product crystallises in needles, and has m. p. 112°. J. J. S.

Reactions and Decomposition of Tetra-alkyl-ammonium Compounds. Ernst von Meyer (*Abhandl. Math.-phys. Klasse Sächs Ges. Wiss.*, 1909, **31**, 179—192).—A detailed account of numerous experiments relating to the reactions which occur when tetra-alkyl-ammonium compounds are treated with aromatic sulphinic acids, potassium thiocyanate, benzoic acid, sodium phenoxide, and other reagents.

The general procedure was to heat equimolecular quantities together in aqueous solution with the addition of sodium hydroxide, distil to dryness, and then continue the heating at 200° on an oil-bath and finally treat the cooled product with alcohol.

The following new compounds are mentioned: p-*Tolylmethylsulphone*, $CH_3 \cdot SO_2 \cdot C_7H_7$, m. p. 86°; p-*tolylethylsulphone*, m. p. 57°; p-*tolylbenzylsulphone*, $CH_2Ph \cdot SO_2 \cdot C_6H_4Me$, m. p. 144·5°; *phenyl benzyl ether*, $C_6H_5 \cdot O \cdot CH_2Ph$, m. p. 39°, b. p. about 280°.

F. M. G. M.

Preparation of Ethers. Joseph Zeltner and B. Tarassoff (*Ber.*, 1910, **43**, 941—945).—The interaction of *s*-dichloro- or dibromomethyl ether and organo-magnesium compounds in dry ether leads to the formation of ethers of the type $CH_2 \cdot R \cdot O \cdot CH_2R'$. *iso*Amyl ether and benzyl ether have been thus prepared, and also the following new compounds: *s-Diphenylethyl ether*, $O(CH_2 \cdot CH_2Ph)_2$, b. p. 194—195°/20 mm., from magnesium benzyl chloride and *s*-dichloromethyl ether. *Benzyl propyl ether*, $CH_2Ph \cdot OPr^{\alpha}$, b. p. 203·5—204·5°/752 mm. (corr.), from bromobenzene, ethyl bromide, magnesium, and *s*-dichloromethyl ether. s-*Dinaphthylmethyl ether*, $(C_{10}H_7 \cdot CH_2)_2O$, m. p. 117°. p-*Xylyl ether*, $(C_6H_4Me \cdot CH_2)_2O$, m. p. 61·5—62·5°, b. p. 310—311° (corr.), and the corresponding *o-xylyl* ether, b. p. 201—203°/24 mm., $D_4^{19\cdot8}$ 1·02189, $n_D^{19\cdot8}$ 1·55784, from *p*- and *o*-bromotoluene respectively. Hydriodic acid, D 1·70, converts the last two ethers almost quantitatively into iodo-*p*-xylene, m. p. 45·5—46·5°, and iodo-*o*-xylene, m. p. 34°, respectively. C. S.

1 : 2-Phenylmethylglycols [*α*-Phenylpropylene *αβ*-Glycols]. Theodor Zincke and K. Zahn (*Ber.*, 1910, **43**, 849—855. Compare Zincke, Abstr., 1884, 1003).—The dibromopropylbenzene used for the preparation of the two phenylpropylene glycols has the constitution previously ascribed to it (*loc. cit.*, 1004), as it can be obtained by the addition of bromine to propenylbenzene (Klages, Abstr., 1903, i, 329). Both glycols are formed at the same time, but the proportions depend upon the conditions of the experiment. Both are racemic compounds, but so far have not been resolved into active components. The *α*-glycol has m. p. 56—57°, and is best prepared by heating the dibromo-compound with potassium acetate and glacial acetic acid, and then hydrolysing the resulting acetate with alcoholic potash. When benzoylated by means of benzoic anhydride or benzoyl chloride, each glycol yields a mixture of the two benzoyl derivatives.

The *α-benzoate*, $C_{23}H_{20}O_4$, crystallises in fibrous masses, m. p. 76—77°, and the isomeric *β-compound* in small needles, m. p. 101°. When hydrolysed, each benzoate yields the corresponding glycol. The same dibromo-derivative is formed when the two glycols react with phosphorus pentabromide. When heated with dehydrating agents, both glycols yield the same pinacolin, namely, benzyl methyl ketone,

$$CH_3\cdot CO\cdot CH_2\cdot C_6H_5,$$

b. p. 214—215°. The phenylhydrazone has m. p. 86—87°, and the semicarbazone, m. p. 194—195° (compare Tiffeneau, Abstr., 1906, i, 663).

Benzaldehyde and acetaldehyde are formed when either of the two glycols is oxidised with chromic acid or permanganate. Nitric acid oxidises the glycols to the *ketonic alcohol*, COPh·CHMe·OH or

$$OH\cdot CHPh\cdot COMe,$$

which is a yellow oil, b. p. 240—242°. The *semicarbazone* crystallises in needles, and has m. p. 184—185° (decomp.), and the *benzoate*,

$$C_{16}H_{14}O_3,$$

has m. p. 109—110°. When further oxidised, the ketonic alcohol yields the diketone, COPh·COMe (compare von Pechmann and Müller, Abstr., 1888, 1087). J. J. S.

Formation of an Ethylene Oxide from the Ammonium Base of Hydroxydiphenylethylamine. Paul Rabe and Julius Hallensleben (*Ber.*, 1910, **43**, 884—886).—*β*-Hydroxy-*αβ*-diphenylethylamine by treatment with methyl iodide (3 mols.) and sodium methoxide (2 mols.) in methyl-alcoholic solution yields a *methiodide*,

$$OH\cdot CHPh\cdot CHPh\cdot NMe_3I,$$

m. p. 194°, from which, by means of water and silver oxide, a solution of the ammonium base is obtained; this solution yields trimethylamine and *diphenylethylene oxide*, m. p. 69°, by warming.

Erlenmeyer's stereoisomeric *iso*hydroxydiphenylethylamine (Abstr., 1899, i, 760) by similar treatment yields a *methiodide*, m. p. 219°, from the base of which a stereoisomeric iso*diphenylethylene oxide*, m. p. 42°, is obtained. The two oxides have a neutral reaction, do not give a coloration with alcoholic ferric chloride, and are unaffected by Fehling's solution, ammoniacal silver solutions, or dilute potassium permanganate. C. S.

The Cholesterol Group. VII. The Phytosterol of the Oil of the Ordinary Walnut (Juglans regia). Angelo Menozzi and A. Moreschi (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 187—192. Compare this vol., i, 254).—One hundred kilos. of walnuts with shells gave 38·4 kilos. of shell-free product, and this, on extraction with ether, yielded 23·2 kilos. of oil. The latter contains 0·26% of a non-saponifiable substance, which forms monoclinic crystals, m. p. 138°, $[\alpha]_D^{14}$ −33·76°, and gives the colour reactions of the members of the cholesterol group. The analytical numbers agree with the formula $C_{26}H_{43}\cdot OH$(or $C_{27}H_{45}\cdot OH$) + H_2O, and in freezing naphthalene the mol. wt. of the hydrated compound is 394. These characters correspond well with those given by Mugge (*Zeitsch. Nahr. Genussm.*, 1898, 1, 45) for phytosterol from cotton-seed oil. The

formate, $H\cdot CO\cdot O\cdot C_{27}H_{45}$ or $H\cdot CO\cdot O\cdot C_{26}H_{43}$, forms elongated laminæ, m. p. 106°, $[\alpha]_D^{20}$ −45·0°; the acetate, prismatic needles, m. p. 121°, $[\alpha]_D^{17}$ −40·48°; the benzoate, small, orthorhombic [Artini: $a:b:c=0{\cdot}716:1:0{\cdot}217$] plates, m. p. 150°, $[\alpha]_D^{17}$ −14·27°, and the salicylate, crystals, m. p. 155°, $[\alpha]_D^{15}$ −50·82°, which are distinguished from all other derivatives of phytosterol by their slight solubility in alcohol (compare Golodetz, Abstr., 1908, i, 20). The acetate readily takes up Br_2, giving the *acetate* of the *dibromide*, $C_{29}H_{48}O_2Br_2$, m. p. 118°.

Dihydrophytosterol, prepared by passing hydrogen through an ethereal solution of phytosterol in presence of platinum black, has m. p. 136—137°, $[\alpha]_D^{20}$ +22·97°, and does not give the ordinary colour reaction with sulphuric acid and chloroform. Its *acetate* has m. p. 134—135°, $[\alpha]_D^{19}$ +14·27°.

Certain of the above physical data are identical with those of a phytosterol which is widespread in the vegetable kingdom.

T. H. P.

Catalysis of Aromatic Acids. Jean B. Senderens (*Compt. rend.*, 1910, 150, 702—704. Compare Abstr., 1909, i, 286, 627; this vol., i, 11, 179).—A further study of the catalytic decomposition of acids, whereby ketones are produced. The oxides of chromium, aluminium, zinc, and calcium behave towards mixtures of benzoic acid and aliphatic acids in the same way as in the case of the aliphatic acids previously examined. The dioxides of cerium, titanium, and tin are very inferior to thorium dioxide in catalytic activity. The latter substance is more rapid in its action than uranium dioxide, and more regular than zirconium oxide.

Aromatic acids, in which the carboxyl group is directly attached to a benzene or naphthalene nucleus, do not give ketones, unless mixed with an aliphatic acid, when a mixed ketone is produced. Those acids, however, in which the carboxyl group is attached to the side-chain are readily converted into the corresponding ketones; thus phenylacetic acid yields αγ-diphenylacetone, whilst phenylpropionic acid furnishes αε-diphenylpentan-γ-one. W. O. W.

Preparation of Nitrogen Derivatives of Phenylglycine-*o*-carboxylic Acid. Badische Anilin- & Soda-Fabrik (D.R.-P. 216748).—When derivatives of anthranilic acid of the general formula (I), where R is an aromatic residue, R′ an aryl, alkyl, or substituted $\cdot CH_2\cdot CN$ or $CH_2\cdot CO_2H$ group, react with formaldehyde, compounds of the general formula (II) are produced, which on treatment with hydrogen cyanide yield products (III), and these on hydrolysis are converted into phenylglycinecarboxylic acids (IV):

$$\underset{\text{(I.)}}{CO_2H\cdot R\cdot NHR'} \qquad \underset{\text{(II.)}}{CO\!<\!\begin{matrix}R\cdot NR'\\ |\\ O\cdot CH_2\end{matrix}} \qquad \underset{\text{(III.)}}{CO_2H\cdot R\cdot NR'\cdot CH_2\cdot CN}$$

$$\underset{\text{(IV.)}}{CO_2H\cdot R\cdot NR'\cdot CH_2\cdot CO_2H.}$$

Anthranilodiacetic acid, $CO_2H\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)_2$, is prepared by

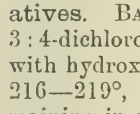
the following series of operations: ω-cyanomethylanthranilic acid is warmed at 70—80° with formaldehyde, and the resulting anhydroformaldehyde compound (m. p. 104—106°) is treated with aqueous potassium cyanide at the ordinary temperature; on addition of mineral acid, the *di-ω-cyanodimethylanthranilic acid* separates; it forms flat prisms, m. p. 168—171° (decomp.), and on alkaline hydrolysis yields the foregoing acid.

Phenylglycine-*o*-carboxylic acid on analogous treatment yields a colourless, crystalline *condensation product*, m. p. 145—148°; the *nitrile*, $CO_2H{\cdot}C_6H_4{\cdot}N(CH_2{\cdot}CO_2H){\cdot}CH_2{\cdot}CN$, is a crystalline powder, m. p. 140° (decomp.).

Diphenylglycine-o-carboxylic acid, prepared from phenylanthranilic acid, forms colourless prisms or needles, m. p. 165—167°.

These substances are employed for the production of indigotin derivatives. F. M. G. M.

Preparation of Anthranilodi-ω-acetic Acid and its Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 216749).—When 3 : 4-dichlorophthalic anhydride (or a mixture of isomerides) is treated with hydroxylamine, it yields 3 : 4-*dichlorophthalylhydroxylamine*, m. p. 216—219°, the more soluble 4 : 5-*dichlorophthalylhydroxylamine* remaining in solution. On hydrolysis, a mixture of 5 : 6- (chiefly) with some 3 : 4-dichloroanthranilic acid is obtained, separation being effected by boiling with dilute ammonium hydroxide and acidifying, when 3 : 4-*dichloroanthranilic acid*, m. p. 240—242°, separates from the hot liquid; on cooling, the more soluble 5 : 6-*dichloroanthranilic acid* crystallises out, m. p. 175—180°.



The inner *dianhydride* of the *methyl ether* (annexed formula), m. p. 151—152°, is prepared by treating 5 : 6-dichloroanthranilic acid (206 parts) in methyl alcoholic solution with 30% formaldehyde (250 parts); the *ethyl ether* forms needles, m. p. 123—124°.

ω-Cyanomethylanhydroformaldehyde-5 : 6-dichloroanthranilic acid [5 : 6-*dichlorodihydro*-2 : 4-*benzoxazin*-1-*one*-4-*acetonitrile*],

$$C_6H_2Cl_2{<}\begin{matrix}N(CH_2{\cdot}CN)\\ CO\text{———}O\end{matrix}{>}CH_2,$$

is formed when the preceding dianhydride compound (262 parts) is treated with cold potassium cyanide (80 parts); it is insoluble in sodium carbonate, and has m. p. 169—172°; on hydrolysis it yields 3 : 4-*dichlorophenylglycine*-2-*carboxylic acid*, m. p. 200°.

5 : 6-*Dichloroanthranilodi-ω-acetonitrile*,

$$CO_2H{\cdot}C_6H_2Cl_2{\cdot}N(CH_2{\cdot}CN)_2,$$

is obtained by treating the corresponding mononitrile with potassium cyanide and acidifying.

5 : 6-*Dichloroanthranilodiacetic acid*, $CO_2H{\cdot}C_6H_2Cl_2{\cdot}N(CH_2{\cdot}CO_2H)_2$, needles, m. p. 190° (decomp.), is prepared by boiling the preceding dinitrile (262 parts) with sodium hydroxide (150 parts) until the ammonia is completely evolved.

The preparations of several compounds previously described are recapitulated. F. M. G. M.

Preparation of Carboxyarylsulphoxidoacetic Acids. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 216725).—The arylthioglycol-*o*-carboxylic acids of the general formula

$$CO_2H\cdot R\cdot S\cdot CH_2\cdot CO_2H$$

are readily oxidised by sodium hypochlorite to the corresponding carboxyarylsulphoxidoacetic acids, $CO_2H\cdot R\cdot SO\cdot CH_2\cdot CO_2H$.

o-Carboxyphenylsulpho-oxidoacetic acid, $CO_2H\cdot C_6H_4\cdot SO\cdot CH_2\cdot CO_2H$, colourless crystals, m. p. 177°, is thus prepared from sodium phenylthioglycol-*o*-carboxylate. F. M. G. M.

Cinnamic Acids. Emil Erlenmeyer and G. Hilgendorff (*Ber.*, 1910, **43**, 955—958).—The results obtained by Riiber and Goldschmidt (this vol., i, 174) do not differ materially from those described by the authors (Abstr., 1909, i, 156, 648). C. S.

Partial Hydrolysis of Proteins. Emil Abderhalden and Casimir Funk (*Zeitsch. physiol. Chem.*, 1910, **64**, 436—446).—The authors suggest the use of β-naphthalenesulphonyl chloride for the purpose of determining the constitution of a polypeptide. The polypeptide is condensed with the chloride in the usual manner, and the resulting β-naphthalenesulphonyl derivative is subjected to hydrolysis by boiling for two to three hours with 10% hydrochloric acid and the hydrolytic products examined. The β-naphthalenesulphonyl group always remains attached to the terminal amino-acid. If a tyrosinyl group is present in the molecule of the polypeptide, then the *O*-β-naphthalenesulphonyl derivative is found among the products of hydrolysis, unless the tyrosinyl group is the terminal group of the chain of condensed amino-acids, when the disulphonyl derivative of tyrosine is obtained.

The hydrolytic products are most readily separated and isolated by Fischer's esterification method.

β-Naphthalenesulphonyl-glycyl-l-tyrosine,

$C_{10}H_7\cdot SO_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot SO_2\cdot C_{10}H_7$,

sinters at 90°, decomposes at 110°, and does not give a red coloration with Millon's reagent. When hydrolysed, it yields β-naphthalenesulphonylglycine and *β-naphthalenesulphonyltyrosine hydrochloride*, $C_{19}H_{18}O_5NSCl$, which sinters at 100° and melts at 170° (decomp.). The *ester hydrochloride*, $C_{21}H_{22}O_5NSCl$, sinters at 190° and has m. p. 195°.

When the β-naphthalenesulphonyl derivative of silk peptone is hydrolysed and the products are esterified, the following compounds can be isolated: β-naphthalenesulphonylalanine ethyl ester, m. p. 95° (Fischer and Bergell, Abstr., 1903, i, 24), alanine ethyl ester hydrochloride, and *O*-β-naphthalenesulphonyltyrosine ethyl ester hydrochloride.

N-*β-Naphthalenesulphonyltyrosine*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot SO_2\cdot C_{10}H_7,$$

can be prepared as its *sodium* salt by the action of the sulphonyl chloride on an alcoholic solution of sodium tyrosinate. The salt sinters at 150° and decomposes at 175°. The *ethyl* ester, $C_{21}H_{21}O_5NS$, melts at 140° to a turbid liquid, which clarifies at 143°.

The di-β-naphthalenesulphonyl derivative of tyrosine is not hydrolysed when boiled with 10% hydrochloric acid. J. J. S.

[Preparation of Aldehyde Derivative of Hydroxy-aromatic Acids.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 216924).—The preparation of diphenylnaphthylmethane derivatives from hydroxynaphthaldehyde-sulphonic, -carboxylic, or -sulphonyl-carboxylic acids and salicylic acid has previously been described. It is now found that the hydroxyaldehydobenzoic acids will condense in the same manner, yielding leuco-acids, which are then oxidised with *nitrosylsulphuric acid*; the following initial compounds are mentioned in the patent: o-*aldehydo*-p-*cresotic acid*, m. p. 190°; p-*aldehydo*-o-*cresotic acid*, colourless, crystalline powder, m. p. 211°; p-*chloro*-o-*aldehydosalicylic acid*, colourless, crystalline powder, m. p. 201°; 2-*hydroxy*-5-*sulphonyl*-1-*aldehydo*-3-*benzoic acid*, colourless crystals, soluble in water. F. M. G. M.

Common Constitution of the Three Specific Biliary Acids. Fritz Pregl (*Zeitsch. physiol. Chem.*, 1910, **65**, 157—179).—When oxidised with a mixture of chromic and acetic acids, cholic acid forms a dehydrocholic acid, m. p. 178°, $[\alpha]_D$ + 66·76°, whilst from deoxycholic acid a dehydrocholic acid, m. p. 186°, $[\alpha]_D$ + 94·4°, is obtained. When oxidised with nitric acid, both cholic acid and deoxycholic acid yield the same choloidanic acid, $C_{18}H_{28}O_8$, decomp. 324°. This was also obtained from cholalic acid; accordingly, all three biliary acids have the C_{18} residue in common. The mother liquors in each case contained a *compound*, $C_{19}H_{28}O_{10}$, m. p. 230—231°, decomp. 240°, yielding an *ethyl* ester, m. p. 195—196°, identical with diethyl ester of the pentabasic acid described by Letsche (Abstr., 1909, i, 697).

Choloidanic acid, when heated above the melting point, is converted into pyrocholoidanic acid, $C_{15}H_{20}O_4$, m. p. 217°, $[\alpha]_D$ + 45·6°, which is probably ζ-p-*carboxyphenyl*-α-*methylheptoic acid*,

$$CO_2H\cdot C_6H_4\cdot[CH_2]_5\cdot CHMe\cdot CO_2H.$$

Constitutional formulæ are assigned to the three biliary acids. E. F. A.

Carbon Monoxide from Aldehydes. Augustin Bistrzycki and Martin Fellmann (*Ber.*, 1910, **43**, 772—776. Compare Abstr., 1901, i, 701, 716; 1904, i, 315; 1906, i, 135; also Mundici, 1909, i, 719; Dakin, Proc., 1909, **25**, 194).—4-*Hydroxy*-3-*aldehydotriphenylacetic acid*, $CO_2H\cdot CPh_2\cdot C_6H_3(CHO)\cdot OH$, obtained by the condensation of salicylaldehyde and benzilic acid, yields the theoretical amount of carbon monoxide when heated with sulphuric acid at 100°, and leaves 4-*hydroxy*-3-*aldehydotriphenylcarbinol*, $OH\cdot CPh_2\cdot C_6H_3(CHO)\cdot OH$, m. p. 123—124°, which reacts with concentrated sulphuric acid at 120—190° losing carbon monoxide. Other aldehydes also react with hot sulphuric acid, the general results obtained so far indicate that whereas benzaldehyde yields but little carbon monoxide when heated with concentrated sulphuric acid, substituted benzaldehydes containing hydroxyl or methyl groups in the ortho- or para-positions evolve carbon dioxide readily. The same substituents in the meta-position do not

facilitate the evolution of carbon monoxide. *o*-Phthaldehydic acid does not yield carbon monoxide. The only aliphatic aldehyde investigated yields little carbon monoxide, but undergoes complex oxidation. J. J. S.

Preparation of Aminoaldehydes. Chemische Werke vorm. Dr. Heinrich Byk (D.R.-P. 217385).—The direct reduction of aromatic carboxylic acids to the corresponding aldehydes has not been recorded previously, and it is found that aminocarboxylic esters can be reduced by nascent hydrogen in either acid or neutral solution to aminoaldehydes. By this method the aldehydes of primary amines, imino-derivatives, nitriles, and tetra-alkylammonium compounds have been prepared, the reaction being general for aliphatic, aromatic, or heterocyclic compounds; the amino-group may be in the nucleus or in the side-chain, and there may be more than one acidic group present.

As reducing agents, sodium, aluminium, or calcium amalgams, magnesium powder, zinc dust, iron filings, or stannous chloride are employed.

The preparation of the aminoaldehyde from ethylglycine in aqueous solution with sodium amalgam is described, also of hydroxyphenylaminopropaldehyde with calcium amalgam, and the method is recommended for the preparation of aspartaldehyde, serinaldehyde, *iso*serinaldehyde, phenyl-α-aminopropaldehyde, α-β-diaminopropaldehyde, pyrrolidinealdehyde, and aminophenylacetaldehyde, $NH_2 \cdot CHPh \cdot CHO$.

F. M. G. M.

New Method for Synthesis of Unsaturated Ketones. Georges Darzens (*Compt. rend.*, 1910, **150**, 707—710).—When *cyclo*hexene is treated with aluminium chloride and acetyl chloride in presence of carbon disulphide, combination occurs between the hydrocarbon and the acid chloride, and a compound is formed to which the constitution $\begin{matrix} CH_2 \cdot CH_2 \cdot CHCl \\ | \qquad\quad | \\ CH_2 \cdot CH_2 \cdot CH \cdot COMe \end{matrix}$ is ascribed.

This forms a stable, complex compound with the aluminium chloride. On treating the product with a tertiary base, such as dimethylaniline, hydrogen chloride and tetrahydroacetophenone are produced. The latter is obtained in 50% yield if stannic chloride is substituted for aluminium chloride.

This condensation is an instance of what appears to be a perfectly general reaction, of which the Friedel and Crafts' reaction is only a particular case. The essential condition appears to be the presence of a double ethylenic linking.

The chlorides of boron, iron, and antimony may be substituted for aluminium chloride, but not with advantage. The chlorides of sulphur, silico , copper, and mercury are without action. Titanium tetrachloride gives good yields.

The author has prepared by this method a large number of new aliphatic and hydroaromatic ketones, and has extended the reaction to the condensation of alkyl halides with unsaturated hydrocarbons.

W. O. W.

Stereoisomeric Chloroimino-ketones. Julius Stieglitz and P. P. Peterson (*Ber.*, 1910, 43, 782—787. Compare Stieglitz and Earle, Abstr., 1904, i, 39).—The chloroimino-derivatives of unsymmetrical ketones appear to exist in two stereoisomeric modifications analogous to pairs of stereoisomeric ketoximes. This is shown in the case of the α- and *β-chloroimides* of *p-chlorbenzophenone*,

$$C_6H_4Cl\cdot CPh{:}NCl.$$

The α-compound crystallises in thin plates, m. p. 104°, and is not so soluble in a mixture of chloroform and light petroleum as the β-compound, which can be isolated as large crystals or as thin prisms and needles when its solution is cooled to −10°. It has m. p. 55°. The compounds are prepared by the action of hypochlorous acid on the corresponding benzophenoneimine; they do not undergo the Beckmann transformation, but their structural identity is shown by the fact that they both react with dry hydrogen chloride, yielding *p*-chlorobenzophenoneimide hydrochloride, which with water is decomposed into ammonium chloride and *p*-chlorobenzophenone. J. J. S.

New Isomerisation of Benzopinacolins and Le Chatelier's Law. Maurice Delacre (*Bull. Soc. chim.*, 1910, [iv], 7, 163—166. Compare Abstr., 1891, 456; 1902, i, 179; 1906, i, 518; 1907, i, 581, 999; 1908, i, 243; 1909, i, 807).—A discussion of the constitution of α- and β-benzopinacolin and the conditions under which these substances undergo isomerisation. W. O. W.

True Constitution of α- and β-Benzopinacolin. Maurice Delacre (*Bull. Soc. chim.*, 1910, [iv], 7, 167—171. Compare preceding abstract).—A critical résumé and discussion of previous work. W. O. W.

Intramolecular Atomic Transpositions. X. Influence of the Substituents of the Phenyl Group in the Transformation of α-Benzopinacolins into β-Pinacolins. P. J. Montagne and S. A. Koopal (*Rec. trav. chim.*, 1910, [ii], 14, 136—149. Compare Abstr., 1907, i, 854, and following abstract).—*α-s*-4 : 4′-Dichlorobenzopinacolin, $O<\begin{matrix}CPh\cdot C_6H_4Cl\\ |\\ CPh\cdot C_6H_4Cl\end{matrix}$, is converted by the action of acetyl chloride into a mixture of the two β-pinacolins: $COPh\cdot CPh(C_6H_4Cl)_2$ (40%) and $C_6H_4Cl\cdot CPh_2\cdot CO\cdot C_6H_4Cl$ (60%). In the preparation of 4-chlorobenzophenone by the Friedel and Crafts' reaction, a certain amount of 2-chlorobenzophenone is also formed.

(Jaeger.—2-Chlorobenzophenone is deposited from solutions in petrol in colourless, lustrous needles (or prisms), which are monoclinic-prismatic; $a : b : c = 0{\cdot}4985 : 1 : 0{\cdot}4706$; $\beta = 83°8'$.)

2-Chlorobenzophenoneoxime has m. p. 121°; when treated with phosphorus pentachloride it yields the anilide, $C_6H_4Cl\cdot CO\cdot NHPh$, and therefore has the constitution $\begin{matrix}C_6H_4Cl\cdot C\cdot Ph\\ \|\\ N(OH)\end{matrix}$.

α-s-4 : 4′-*Dichlorobenzopinacolin*, prepared by reducing 4-chlorobenzophenone with zinc dust, acetic acid, and sulphuric acid, has m. p.

220° (decomp.). When no sulphuric acid is added, the reduction yields chiefly the acetate of 4-chlorobenzhydrol.

4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacone is decomposed by alcoholic potassium hydroxide into 4 : 4′-dichlorobenzophenone and 4 : 4′-dichlorobenzhydrol. A blue colour appears during the reaction, and a similar colour is given by benzopinacone, *s*-4 : 4′-dichlorobenzopinacone, and *s*-4 : 4′-dibromobenzopinacone, but not by *α*-4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacolin and *α*-4 : 4′-dichlorobenzopinacolin. R. V. S.

Intramolecular Atomic Transpositions. XI. Influence of the Substituents of the Phenyl Group in the Transformation of Benzopinacones into Benzopinacolins. P. J. Montagne (*Rec. trav. chim.*, 1910, [ii], 14, 150—162. Compare preceding abstract).—The action of acetyl chloride on 4 : 4′-*dibromobenzopinacone*, $C_6H_4Br\cdot CPh(OH)\cdot CPh(OH)\cdot C_6H_4Br$, yields a mixture of the two pinacolins: $C_6H_4Br\cdot CPh_2\cdot CO\cdot C_6H_4Br$ (57—58%) and $COPh\cdot CPh_2\cdot C_6H_4Br$ (42—43%) (compare Abstr., 1907, i, 854). The dibromobenzopinacone is prepared by reducing *p*-bromobenzophenone with zinc dust and acetic acid; it has m. p. about 178° (decomp.). The Friedel and Crafts' reaction with *p*-bromobenzoyl chloride and bromobenzene leads to the production of some 2 : 4′-dibromobenzophenone in addition to the 4 : 4′-dibromo-compound, which is the main product. 2 : 4′-Dibromobenzophenone has m. p. 62° (Heidenreich, Abstr., 1894, i, 417, gave 51—52°) and b. p. 381—384°/764 mm.

(Jaeger.—The substance forms large, lustrous, transparent crystals, of which the symmetry is monoclinic-prismatic; $a : b\ c = 1{\cdot}0962 : 1 : 0{\cdot}5951$; $\beta = 68°25\frac{1}{2}'$.

4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacolin is deposited from a mixture of ethyl acetate and petrol in flat, colourless crystals of monoclinic-prismatic symmetry; $a : b : c = 1{\cdot}2853 : 1 : 1{\cdot}0665$; $\beta = 63°47'$.)

R. V. S.

Action of Ammonia on Tetramethyl*cyclo*butandione. Edgar Wedekind and M. Miller (*Ber.*, 1910, 43, 834—836).—*Iminotetramethyl*cyclo*butanone*, $CMe_2<\begin{matrix}C(:NH)\\CO\end{matrix}>CMe_2$, is formed when tetramethyl*cyclo*butane-1 : 3-dione (Wedekind and Weisswange, Abstr., 1906, i, 437) is heated with 20% ammonium hydroxide solution at 120—130°. It crystallises in glistening, felted needles, m. p. 108·5°, dissolves readily in mineral acids, yields a *phenylhydrazone*, $C_{14}H_{19}N_3$, m. p. 162°, and is hydrolysed to the original diketone when heated with concentrated hydrochloric acid at 120—130°. J. J. S.

New Type of Quinhydrone Compound. Angelo Knorr (*Ber.*, 1910, 43, 798—800).—Quinone mono- and di-chloroimides form additive compounds with quinol. These resemble quinhydrone in appearance, composition, and in the readiness with which they dissociate in solution.

Quinol quinonechloroimide, $C_6H_6O_2,C_6H_4ONCl$, crystallises in blackish-green needles with a metallic lustre; it decomposes at 119°, and is resolved into its components when warmed with benzene.

Quinol quinonedichloroimide, $C_6H_6O_2,C_6H_4N_2Cl_2$, crystallises in large, blackish-green needles, which decompose at 129—130°.

Benzidine quinonedichloroimide, $2C_{12}H_{12}N_2,C_6H_4N_2Cl_2$, crystallises in deep violet-coloured needles, which decompose at 121°. J. J. S.

Preparation of Halogenated 2-Methylanthraquinone Derivatives Substituted either in the Aromatic Nucleus or in the Side-Chain. Badische Anilin- & Soda-Fabrik (D.R.-P. 216715).—Bromomethylanthraquinones have been prepared previously as crystalline substances, which, on heating with alkalis at 180—200°, yielded methylalizarins identical with those prepared by the sulphonation of the corresponding methylanthraquinones and subsequent fusion with alkali.

Bromo-2-methylanthraquinone, m. p. 200—202°, is prepared by heating 2-methylanthraquinone (10 parts) with bromine (8 parts) in a sealed tube at 170° during six hours; if twice the quantity of bromine is employed, a *dibromomethylanthraquinone* is formed.

2-*Dichloromethylanthraquinone*, m. p. about 200°, is produced, along with a *monochloro*-derivative, when 2-methylanthraquinone is treated with chlorine at 150—160°. The chlorine in the foregoing reaction can be replaced by sulphuryl chloride.

When 4-bromo-1-hydroxy-2-methylanthraquinone is heated at 150—170° with half its weight of bromine during four to six hours, a *ω-bromo*-derivative is obtained, which crystallises from acetic acid in lustrous, golden needles. By analogous methods, mixed halogenated methylanthraquinones can be prepared. F. M. G. M.

Preparation of Sulphur Derivatives of Anthraquinone. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 216480).—By the condensation of thiosalicylic [*o*-thiolbenzoic] acid or its derivatives with α-chloro- and α-bromo-anthraquinones, products having the following general formula are obtained:

$$C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_3\cdot S\cdot C_6H_4\cdot CO_2H = H_2O +$$

$$C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}S\\CO\end{matrix}\!>\!C_6H_4.$$

They form brown powders, which are insoluble in dilute acids, alkalis, or organic solvents, soluble in concentrated sulphuric acid, and do not melt below 350°. F. M. G. M.

A New Process for Obtaining Glycuronic Acid (and Menthylglycuronic Acid). Carl Neuberg and S. Lachmann (*Biochem. Zeitsch.*, 1910, **24**, 416—422).—Menthylglycuronic acid is obtained by administering menthol in the form of an emulsion (obtained by diluting an alcoholic solution with water) to a rabbit. To the acidified urine of the animal is then added one-quarter the volume of alcohol, and one-eighth of that of ether. To the ethereal extract, excess of ammonia is added, and the ammonium salt of the glycuronate separates out. Glycuronic acid can be obtained from the menthyl derivative by hydrolysis with sulphuric acid. The authors also give the preparation and composition of some basic lead salts of menthylglycuronic acid. S. B. S.

Isomeric Borneolglycuronic Acids. Juho Hämäläinen (*Skand. Arch. Physiol.*, 1909, 23, 86—98).—The isomeric borneolglycuronic acids described in this paper were obtained from the urine of rabbits fed on the requisite borneol. Although Magnus-Levy has shown (Abstr., 1907, i, 228) that the animal organism is incapable of differentiating between *d*- and *l*-borneol, nevertheless the borneol resulting from the hydrolysis of the basic lead precipitate obtained from the urine of rabbits fed on *r*-borneol is distinctly lævorotatory. The borneolglycuronic acids are not acted on by emulsin, but are hydrolysed by dried yeast extract (compare, however, the following abstract); the conclusion is drawn, therefore, that these compounds are α-glucosides, and since they do not reduce Fehling's solution, and when hydrolysed yield the corresponding borneol and dextrorotatory glycuronic acid, probably have the constitution represented by the formula: $C_{10}H_{17}O\cdot CH<\begin{matrix}CH(OH)\cdot CH(OH)\\ O\text{———}CH\cdot CH(OH)\cdot CO_2H\end{matrix}$.

r-*Borneolglycuronic acid*, $C_{16}H_{26}O_7$, crystallises with $\frac{1}{2}H_2O$ in small, white needles, m. p. 94—95°; the anhydrous substance is very hygroscopic, and has m. p. 163—165°, $[\alpha]_D^{20}$ −47·93° (in water); the *zinc* salt, $C_{32}H_{50}O_{14}Zn,2H_2O$, forms long, glistening needles, and decomposes at 200° without melting.

r-iso*Borneolglycuronic acid* crystallises with $1H_2O$ in small, white needles, m. p. 104—106°; the anhydrous substance is hygroscopic, and has m. p. 162—163°, $[\alpha]_D^{20}$ −42·62° (in water); when kept for several days in a vacuum desiccator over phosphoric oxide, it partly changes into a *substance*, m. p. 205—206°, which is probably a lactone of the acid; the *zinc* salt ($2H_2O$) forms long, glistening needles, and turns black at 200°, but does not melt.

l-*Borneolglycuronic acid* is extremely hygroscopic, and has m. p. 162—163°, $[\alpha]_D^{20}$ −69·03° (in water); the hydrated acid has m. p. 96—97°; the *zinc* salt ($2H_2O$) forms glistening, white needles, and turns brown at 202° without melting; a *substance*, m. p. 206—208°, probably a lactone of the acid, was obtained as a by-product.

d-*Borneolglycuronic acid* has m. p. 164—165°, $[\alpha]_D^{20}$ −37·02°; the acid crystallises with H_2O in small, white needles, m. p. 94—95°.

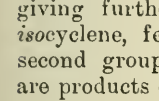
W. H. G.

Fission of Borneol- and Camphor-glycuronic Acids by Enzymes. Juho Hämäläinen (*Skand. Arch. Physiol.*, 1910, 23, 297—301).—The observations recorded in the previous paper (compare preceding abstract) on the behaviour of borneolglycuronic acids towards enzymes are worthless, since the chloroform employed to render the solutions sterile contained hydrogen chloride. The borneolglycuronic acids are hydrolysed very slowly by emulsin, but not by the enzymes of yeast, and are, consequently, to be regarded as β-glucosides.

l-Camphorglycuronic acid in the anhydrous state has m. p. 128—129° (compare Magnus-Levy, Abstr., 1907, i, 228); it is not hydrolysed by dried yeast extract, but when acted on by emulsin yields camphorol and is therefore, undoubtedly, a β-glucoside. W. H. G.

Pinene Hydrohalides and their Transformation into Hydrocarbons of the Santene and Cyclene Types. Iwan L. Kondakoff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 338—355).—The author discusses his own work (compare Abstr., 1908, i, 665; 1909, i, 311, 502, 942) and that of other investigators, more especially on the pinene hydrochlorides, and draws the following conclusions: The solid *d*- and *l*-pinene hydrochlorides do not possess definite optical rotations, and represent mixtures of two antipodes with preponderance of one or the other form. When hydrogen chloride is removed with avoidance of all isomerising influences, the pure *d*-hydrochloride yields almost pure bornylene, whilst the pure *l*-hydrochloride gives camphene (cyclene ?), probably formed as a result of the action of conditions of isomerisation on the cyclene or bornylene representing the first product of the reaction. It is possible that both the hydrochlorides undergo preliminary transformation into *iso*bornyl hydrochloride.

On treatment with halogen hydracids, pinene yields principally two classes of derivatives, firstly, real borneol derivatives, and secondly, real fenchyl compounds, each of these classes of compounds then giving further independent derivatives, such as bornylene, cyclene, *iso*cyclene, fenchobornylene, fenchocyclene, and fencho*iso*cyclene. A second group comprises methene-camphene and *iso*camphene, which are products of isomeric change of compounds of the first series.



When methene-camphene is oxidised, for example, by dilute permanganate solution, it seems to undergo hydration to a tertiary alcohol, which decomposes, giving cyclene, the latter then combining with water to form the annexed secondary alcohol; this, by loss of water, is converted into *iso*camphene. T. H. P.

Essential Oils. Schimmel & Co. (*Bericht*, April, 1910).—The leaves of *Aegle marmalos* yielded 0·6% of a pale yellow oil, D^{25} 0·856, α_D^{26} +10·71°, boiling principally below 130°, and having saponification number 10·6.

Java citronella oil contained about 0·2% of citral. Citronella oil from German New Guinea had D^{15} 0·8964, α_D, −1°20′, and contained 78% of geraniol and citronellal.

Cypress camphor is identical with cedar camphor, and has $[\alpha]_D$ +10°5′ in chloroform.

Dill oil from Galicia had D^{15} 0·9425, α_D +48°16′, n_D^{20} 1·50775, and was not completely soluble in 80% alcohol, and probably contained fennel oil.

Bergamot oil from Sicily had D^{15} 0·8829, α_D +15°20′, acid number 1·5, ester number 100·7, contained 5·8% of non-volatile matter, and gave a clear solution with 0·5 or more volumes of 90% alcohol. Terpinyl acetate has been found as an adulterant recently in bergamot oils, and may best be detected by quantitative fractional distillation of the oil and examination of the optical rotation and refractive index of each portion (compare Umney, *Chem. and Drugg.*, 1909, 75, 411, 487, 522).

A résumé of the results of Chace's investigations on the occurrence

of pinene in lemon oil (*Circ.* No. 46, *Bur. Chem. U.S.A. Dept. Agric.*) is given and of the various criticisms of these results that have appeared in technical journals.

According to Swenholt, oils distilled from the leaves and twigs of the Coniferous trees named below had the following constants: *Picea Engelmanni*, D 0·8950, α_D +1°55′38″ (in a 5-cm. tube), saponification number 24·15, corresponding with 8·5% of bornyl acetate: this oil smells of camphor. *Pinus murrayana* had saponification number 51·87, equal to 18% of bornyl acetate. *P. flexilis* had D 0·8670, α_D +4°28′ (in a 5-cm. tube), saponification number 43·14, corresponding to 15% of bornyl acetate. *P. edulis* had D 0·8653, α_D −3°36′58″ (in a 5-cm. tube), saponification number 17·55, equivalent to 6% bornyl acetate.

Lemon-grass oils from Jalpaiguri, India, had the following constants: I. Grass cut in July, no flowers: D^{15} 0·8924 to 0·8954, α_D −0°28′ to −0°49′, aldehydes (by acid bisulphite process) 87—90%. II. Grass cut in September, no flowers: D^{15} 0·8925, α_D −0°53′, aldehydes 85·5%. III. Leaves of grass, in flower: D^{15} 0·8916, α_D −1°5′, aldehydes 86·0%. IV. Flowers only: D^{15} 0·8897, α_D −1°15′, aldehydes 83%. A lemon-grass oil from Eastern Bengal had D^{15} 0·9122, α_D ±0, aldehydes 83%. A specimen from New Guinea contained 65% of aldehydes, and had D^{15} 0·8857, α_D −0°40; both the latter oils were of the "insoluble" type.

Mosla japonica herb furnished, according to Murayama, 2% of oil containing *p*-cymene and 50% of carvacrol.

Myrtle oil from Cyprus had D^{15} 0·9174, α_D +8°11′, n_D^{20} 1·46357, acid number 0·3, ester number 20·9, acetyl ester number 63·9, and was soluble in one or more volumes of 80% alcohol.

Oil from sweet orange flowers, grown in Southern France, had D^{15} 0·8686, α_D +45°16′, n_D^{20} 1·47352, acid number 1·8, ester number 16·7, and was soluble in 0·5 volume of 90% alcohol, becoming opalescent with 5 volumes.

A so-called "petit-grain" oil, distilled from leaves only in Dominica, had D^{15} 0·8531, α_D +43°36′, acid number 1·2, ester number 6·1, and was soluble in 4 to 5 volumes of 90% alcohol with slight opalescence.

Rosemary oil from Greece had D^{15} 0·9148, α_D +1°37′, and was soluble in one or more volumes of 80% alcohol.

Celery seed oil had D^{15} 0·8946, α_D +67°51′, n_D^{20} 1·48566. The terpene fraction had b. p. 175—180°, and consisted mainly of *d*-limonene. The alcohol fraction had b. p. 195—230°, and was not examined. The portion boiling from 110—130° under 9 mm. pressure consisted mainly of a sesquiterpene (compare Ciamician and Silber, Abstr., 1897, i, 291, 483), which it is proposed to call d-*selinene*. The latter could not be obtained pure by fractionation. The crude sesquiterpene was converted into the *dihydrochloride*, m. p. 72—74°, $[\alpha]_D$ +18° in chloroform, and this, on treatment with sodium ethoxide, yielded a hydrocarbon, b. p. 268—272°, D^{15} 0·9232, D^{20} 0·9196, α_D +49°30′, n_D^{20} 1·50483, which was probably identical with the original selinene, since on treatment with hydrogen chloride it furnished the dihydrochloride melting at 72—74°. No other crystalline derivatives could be obtained. The oil also contained phenols, sedanolide, and sedanonic acid, as found by Ciamician and Silber (*loc. cit.*).

A hydrocarbon fraction of star anise oil had b. p. 63°/13·5 mm., D^{15} 0·8601, α_D −22°31′, n_D^{20} 1·47226, and was found to contain, in addition to the constituents already observed, *p*-cymene and a mixture of *l*-α- and -β-phellandrene. Cineol, safrole, and terpineol were also noted in the alcohol fraction (compare Oswald, Abstr., 1891, i, 957, and Tardy, Abstr., 1903, i, 46).

Two storax oils proved to be merely styrene perfumed with benzyl benzoate; one of them also contained pinene.

"Yellow pine oil," obtained by the steam distillation of yellow pine "stumps," had D^{15} 0·9536, α_D −3°26′, n_D^{20} 1·48537, acid number 0, ester number 14·2, acetyl ester number 161·4, and total alcohol content 58%. *l*-α-Terpineol was isolated from this oil in a pure state (compare Teeple, Abstr., 1908, i, 355). The other constituents were α- and β-pinene, camphene, *l*-limonene, dipentene, γ-terpinene, *l*-borneol, cineol, *i*-fenchyl alcohol, camphor, and methylchavicole. The last four are new constituents as regards oils derived from species of the *Abietineae*, whilst fenchyl alcohol has not been observed in any natural essential oil previously. The oil also contained a *stereoisomeride* of *i*-fenchyl alcohol: this had b. p. 202—203°, D^{15} 0·9655, α_D +1°10′, n_D^{20} 1·47465; on oxidation it yielded *i*-fenchone, and on dehydration a fenchene, having b. p. 154—156°, D^{15} 0·8669, α_D −2°38′, n_D^{20} 1·47056. The *phenylurethane* of the alcohol had m. p. 94—95°, and the *phthalic acid* ester, m. p. 142—144°.

A résumé of recent work on the detection of adulterants in turpentine oil is given (compare Marcusson, *Chem. Zeit.*, 1909, **33**, 966, 978, 985; Herzfeld, *loc. cit.*, 1081; Nicolardot and Clement, *Compt. rend.*, 1909, **49**, 572; Mansier, this vol., ii, 1056; Darmois, Abstr., 1908, ii, 747). *Pinus ponderosa* turpentine, from the Philippines, gave, according to Richmond, 23·4% of turpentine oil, which had D_{30}^{30} 0·8593, α_D^{30} +26·5°, n_D^{30} 1·4656, and boiled mostly from 154° to 165·5°.

Ylang-ylang oil, distilled in Réunion, had D^{15} 0·939, α_D −64°, n_D^{20} 1·510, saponification number 97, and contained benzoic acid 9%, acetic acid 4·0%, alcohols (linalool and geraniol) 25·5%, and cadinene, 31%.

Cinnamomum tamala leaf oil had D^{15} 1·0257, α_D +16°37′, n_D^{20} 1·52596, eugenol 78%, and was soluble in 1·2 or more volumes of 70% alcohol. The oil, after removal of eugenol, had α_D +66°40′, and contained *d*-α-phellandrene.

Guava-leaf oil from Cuba had D^{15} 0·9157, α_D −10°5′, n_D^{20} 1·49638, acid number 2·0, ester number 6·4, and was soluble in 10 volumes of 90% alcohol.

Mentha sylvestris oil, from Cyprus, had D^{15} 0·9701, α_D +31°30′, n_D^{20} 1·49544, acid number 2·4, ester number 20·9, acetyl ester number 171·4, and was soluble in 3 volumes of 70% alcohol. It contained pulegone, menthol, and probably carvacrol. T. A. H.

[Carrot Oil, the Ethereal Oil from Daucus Carota.] Erwin Richter (*Ber.*, 1910, **43**, 958).—The author will reply to Deussen's criticisms (*ibid.*, 523) of his work (Abstr., 1909, i, 943) when the promised fuller details are published. C. S.

Theory of the Cold Vulcanisation of Rubber. F. Willy Henrichsen and Erich Kindscher (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 202—209. Compare this vol., ii, 62).—Experiments have been made to determine the nature of the process of the vulcanisation of rubber with sulphur chloride. Weighed amounts of purified para-rubber were subjected to the action of varying quantities of a dry benzene solution of sulphur chloride in stoppered flasks for a period of three to four weeks, at the end of which time the amount of unchanged sulphur chloride in the clear solution was determined. The observed changes in the concentration of the sulphur chloride indicate that a definite compound is formed of the composition

$$(C_{10}H_{16})_2,S_2Cl_2.$$

Direct analysis of the substance which separates out from the benzene solution gave quantities of sulphur largely in excess of that required by the formula, but this is probably due to decomposition of the sulphur chloride in the processes of separation and purification.

When treated for several days with an alcoholic solution of sodium hydroxide, the above compound loses two molecules of hydrogen chloride, and a dark brown, hard substance of the composition

$$C_{20}H_{30}S_2$$

is obtained. In consequence of the separation of free sulphur, the analytical data for the amount of sulphur present are from 1 to 2% higher than that required by the formula.

The authors consider that ordinary vulcanised rubber consists of a solid or semi-solid solution of para-rubber and the sulphur chloride additive compound, in which variable amounts of adsorbed sulphur are contained. H. M. D.

Phylloporphyrin. Léon Marchlewski (*Annalen*, 1910, **372**, 252—253).—Polemical. A reply to Willstätter and Fritsche (this vol., i, 126). W. H. G.

Phylloporphyrin. Richard Willstätter (*Annalen*, 1910, **372**, 253).—Polemical. A reply to Marchlewski (compare preceding abstract). W. H. G.

Colouring Matter of Tomatoes. Richard Willstätter and Heinrich H. Escher (*Zeitsch. physiol. Chem.*, 1910, **64**, 47—61. Compare Schunck, *Proc. Roy. Soc.*, 1903, **72**, 165; Montanari, Abstr., 1905, i, 293.)—Lycopene, the colouring matter of tomatoes, and carrotene (Abstr., 1907, i, 865) have the same molecular formula, $C_{40}H_{56}$, but are not identical. Lycopene is most readily obtained from preserved tomatoes, together with a small amount of carrotene. It crystallises from light petroleum or a mixture of alcohol and carbon disulphide in pale or dark carmine-red, felted prisms. Its solutions in carbon disulphide have a bluish-red colour, whereas carrotene yields reddish-yellow solutions. It has m. p. 168—169° (corr.) [Montanari (*loc. cit.*) gives 170° (uncorr.)], and is less soluble than carrotene in ether, alcohol, carbon disulphide, or light petroleum. A dilute alcoholic solution has two absorption bands: $\lambda = 510—499$ and $\lambda = 480—468$. Carbon disulphide solutions have two absorption bands

in the green and one in the blue. Lycopene absorbs oxygen much more readily than does carrotene, and to the extent of 32·5%. Its di-iodide, $C_{40}H_{56}I_2$, forms a dark green, gelatinous precipitate. A carbon disulphide solution of lycopene reacts with bromine, yielding the *compound*, $C_{40}H_{44}Br_{26}$, which sinters at 148° and decomposes at 174°.

When carrotene is exposed to oxygen, an odour of violet roots is noticed. In addition to the di-iodide described by Willstätter and Mieg, carrotene yields the *compound*, $C_{40}H_{56}I_2$, which crystallises in dark violet plates with a metallic lustre, m. p. 136—137°. Carrotene and bromine yield the compound $C_{40}H_{36}Br_{22}$, which decomposes at 171—174°. Xanthophyll yields a similar bromide, $C_{40}H_{40}Br_{22}$.

J. J. S.

The Action of Zinc Oxide on Tannin. Leo F. Iljin (*J. pr. Chem.*, 1910, [ii], **81**, 327—328. Compare Abstr., 1909, i, 821).—If 100 grams of tannin are dissolved in a litre of water, boiled for four hours with 100 grams of zinc oxide, and filtered, the filtrate is slightly coloured and does not react with ferric chloride. The residue, after decomposition with sulphuric acid, yields 35 grams of gallic acid, and 32 grams of the same compound as was obtained by the action of zinc dust on tannin.

C. H. D.

Basic Properties of Oxygen. Compounds of Dimethylpyrone and the Halogen Hydrides. Douglas McIntosh (*J. Amer. Chem. Soc.*, 1910, **32**, 542—547).—In an earlier paper (Abstr., 1908, i, 596) it has been shown that certain substances regarded by Baeyer and Villiger (Abstr., 1901, i, 658; 1902, i, 112, 355) as quadrivalent oxygen compounds are either solid solutions or molecular compounds containing alcohol of crystallisation. Since it is possible that the salts of dimethylpyrone might be considered as compounds containing "acid of crystallisation," some of these have now been examined over a wide range of temperature.

Conductivity measurements of dimethylpyrone in liquid hydrogen bromide at $-78°$ and in liquid hydrogen chloride at $-100°$ have been made, and the results are tabulated and plotted as curves. It is shown that the molecular conductivity increases with the concentration, and the conclusion is therefore drawn that complex ions are formed.

In addition to the salts described by Collie and Tickle (Trans., 1899, 75, 710), the following have now been obtained: $C_7H_8O_2,3HCl$, m. p. $-25°$; $C_7H_8O_2,4HBr$, m. p. $-59°$; $C_7H_8O_2,2HBr$, m. p. $-2°$; $C_7H_8O_2,4HI$, m. p. $-42°$; $C_7H_8O_2,2HI$, m. p. 7°. Weinland and Reischle (Abstr., 1908, i, 974) have described two dimethylpyrone hydrofluorides, but experiments which are now described indicate that, if such compounds are formed, they are very unstable.

Suggestions are made with reference to the constitution of the compounds of dimethylpyrone with the halogen hydrides.

E. G.

***o*-*ψ*-Bromides from *o*-Hydroxystyrene, their Transformation Products, and Conversion into Coumaran Derivatives.** Karl Fries and Paul Moskopp (*Annalen*, 1910, **372**, 187—204).—An

investigation on the ψ-bromides of *o*-ethylphenol which result from the action of bromine on *o*-hydroxystyrene.

3 : 5-*Dibromo*-2-*hydroxystyrene bromide*, $OH\cdot C_6H_2Br_2\cdot CHBr\cdot CH_2Br$, is formed by the action of bromine on a solution of *o*-hydroxystyrene in glacial acetic acid; it crystallises in aggregates of plates, m. p. 108°, and is converted (1) by acetic anhydride and concentrated sulphuric acid into the *acetate*, $C_{10}H_8O_2Br_4$, white needles, m. p. 74°; (2) by boiling acetic anhydride and anhydrous sodium acetate into β : 3 : 5-*tribromo*-α : 2-*diacetoxyethylbenzene*,

$$OAc\cdot C_6H_2Br_2\cdot CH(OAc)\cdot CH_2Br,$$

colourless plates, m. p. 90°; (3) by methyl alcohol, under pressure at 100°, into β : 3 : 5-*tribromo*-2-*hydroxy*-α-*methoxyethylbenzene*,

$$OH\cdot C_6H_2Br_2\cdot CH(OMe)\cdot CH_2Br,$$

large, white, rhombic crystals, m. p. 58°, which, when boiled with glacial acetic acid, acetic anhydride, and sodium acetate, yield 4 : 6-*dibromo*-2-*methoxycoumaran*, $C_6H_2Br_2<\begin{matrix}CH(OMe)\\O\end{matrix}>CH_2$, white, spear-shaped needles, m. p. 95°; (4) by zinc and hydrochloric acid into 3 : 5-*dibromo*-2-*hydroxystyrene*, $C_8H_6OBr_2$, slender needles, m. p. 58°, the *acetate* of which, $C_{10}H_8O_2Br_2$, crystallises in needles, m. p. 51°; and (5) by hot glacial acetic acid and anhydrous sodium acetate into 4 : 6-*dibromo*-2-*acetoxycoumaran*, $C_{10}H_8O_3Br_2$, rhombic plates, m. p. 98—99°, which when treated with an aqueous-alcoholic solution of sodium hydroxide yields 4 : 6-*dibromo*-2-*hydroxycoumaran*, $C_8H_6O_2Br_2$, slender needles, m. p. 120°; the latter substance, dissolved in light petroleum, is converted by phosphoric oxide into 4 : 6-dibromocoumarone (compare Simonis and Wenzel, Abstr., 1900, i, 231).

4 : 6-*Dibromo*-2-*coumaranone*, $C_6H_2Br_2<\begin{matrix}CO\\O\end{matrix}>CH_2$, is formed by the action of chromic acid on 4 : 6-dibromo-2-hydroxycoumaran; it crystallises in pale yellow needles, m. p. 145°, and (1) condenses with isatin in glacial acetic acid containing concentrated sulphuric acid, yielding 1-(4 : 6)-*dibromocoumaranonyl*-3-*indole*,

$$C_6H_2Br_2<\begin{matrix}CO\\O\end{matrix}>C:C<\begin{matrix}C_6H_4\\CO\end{matrix}>NH,$$

brownish-red needles, m. p. above 280°; (2) is converted by glacial acetic acid and sodium nitrite into 4 : 6-*dibromo*-1-*oximinocoumaranone*, $C_8H_3O_3NBr_2$, compact, glistening, yellow prisms, m. p. 186° (decomp.), which when boiled with acetic acid and hydrochloric acid yields 3 : 5-*dibromo*-2-*hydroxyphenylglyoxylic acid*,

$$OH\cdot C_6H_2Br_2\cdot CO\cdot CO_2H,$$

compact, yellow needles, m. p. 142° (decomp.); the latter compound condenses with *o*-phenylenediamine, yielding the corresponding *quinoxaline* derivative, which crystallises in needles, m. p. above 280°.

α : β : β : 3 : 5-*Pentabromo*-2-*hydroxyethylbenzene*,

$$OH\cdot C_6H_2Br_2\cdot CHBr\cdot CHBr_2,$$

is formed by heating 3 : 5-dibromo-2-hydroxystyrene bromide with bromine under pressure at 100°; it crystallises in white nodules, m. p. 141°; the *acetyl* derivative, $C_{10}H_7O_2Br_5$, forms crystalline nodules, m. p. 128°. The pentabromo-compound is converted (1) by hot glacial acetic acid and anhydrous sodium acetate into β : β : 3 : 5-*tetrabromo*-

2-*hydroxy*-α-*acetoxyethylbenzene*, $C_{10}H_8O_3Br_4$, plates, m. p. 126°; (2) by hot acetic anhydride and anhydrous sodium acetate into β : β : 3 : 5-*tetrabromo*-α : 2-*diacetoxyethylbenzene*, $C_{12}H_{10}O_4Br_4$, small, glistening, white plates, m. p. 115°; (3) by methyl alcohol at 100° into β : β : 3 : 5-*tetrabromo*-2-*hydroxy*-α-*methoxyethylbenzene*, $C_9H_8O_2Br_4$, large, white plates, m. p. 110°; and (4) by zinc and hydrochloric acid into ω : 3 : 5-*tribromo*-2-*hydroxystyrene*, $C_8H_5OBr_3$, crystalline nodules, m. p. 95°, the *acetate* of which, $C_{10}H_7OBr_3$, crystallises in small prisms, m. p. 132°; the *methyl ether* crystallises in leaflets, m. p. 64°, and when oxidised yields 3 : 5-dibromo-2-methoxybenzoic acid. W. H. G.

o-ψ-Bromides of Thymol and 4-Hydroxy-1-methyl-3-*iso*propylbenzene (4-Hydroxy-*m*-cymene), their Transformation Products, and Conversion into Coumaran and Coumaranone Derivatives. Karl Fries (*Annalen*, 1910, **372**, 205—236).—The bromination of 2-hydroxy-α : 4-dimethylstyrene leads to the formation of a hexabromo-ψ-bromide of thymol, identical with the hexabromothymol obtained by von Baeyer and Seuffert (Abstr., 1901, i, 216) from menthone (compare Fries and Fickewirth, Abstr., 1908, i, 160). The formulæ assigned by the first-named investigators to this compound and its derivatives are incorrect; it is shown that the hexabromo-compound has the constitution: $CBr{:}CH{-}\underset{\|}{C}{\cdot}CBr(CH_2Br){\cdot}CHBr_2$
$CMe{:}CBr{\cdot}\underset{|}{C}{\cdot}OH$

[With W. Volk.]—α : β : β : 2 : 6-*Pentabromo*-3-*hydroxy*-1-*methyl*-α-*bromomethyl*-4-*ethylbenzene* is most readily prepared by the action of bromine on a solution of thymol in chloroform; it is converted by sodium hydrogen carbonate into β : β : 3 : 5-*tetrabromo*-2-*hydroxy*-4-*methyl*-α-*bromomethylstyrene*, m. p. 106° (102° : von Baeyer and Seuffert, *loc. cit.*), and by an aqueous-alcoholic solution of sodium hydroxide into 1 : 4 : 6-*tribromo*-5-*methyl*-2-*bromomethylcoumarone*, m. p. 179°. The latter substance is converted by a solution of hydrogen bromide in glacial acetic acid into 1 : 1 : 4 : 6-*tetrabromo*-5-*methyl*-2-*methylene-coumaran*, $C_6HMeBr_2\langle\begin{matrix}C(:CH_2)\\ O\end{matrix}\rangle CBr_2$, which crystallises in prisms, m. p. 140°, and is converted (1) by silver acetate in hot glacial acetic acid into 1 : 4 : 6-*tribromo*-1-*acetoxy*-5-*methyl*-2-*methylenecoumaran*, $C_{12}H_9O_3Br_3$, small needles, m. p. 138°; (2) by methyl alcohol under pressure at 100° into 1 : 4 : 6-*tribromo*-1-*methoxy*-5-*methyl*-2-*methylenecoumaran*, $C_{11}H_9O_2Br_3$, which forms slender needles, m. p. 148°, and, when treated with cold concentrated sulphuric acid, yields 4 : 6-*dibromo*-5-*methyl*-2-*methylene-coumaran*-1-*one*, $C_6HMeBr_2\langle\begin{matrix}C(:CH_2)\\ O\end{matrix}\rangle CO$, slender, white needles, m. p. 145°; the acid, of which the latter compound is the lactone, could not be isolated, but the *methyl* ester was prepared; it forms small needles, m. p. 119°.

β : β : 3 : 5-Tetrabromo-2-hydroxy-4-methyl-α-bromomethylstyrene is converted by methyl alcohol at 100° into β : 3 : 5-*tribromo*-2-*hydroxy*-β-*methoxy*-4-*methyl*-α-*bromomethylstyrene*, $OH{\cdot}C_6HMeBr_2{\cdot}C(CH_2Br){:}CBr{\cdot}OMe$,

which crystallises in long prisms, m. p. 85°, and, when treated with hydrogen iodide in glacial acetic acid, yields *β* : 3 : 5-*tribromo β-iodo*-2-*hydroxy*-4-*methyl*-*α*-*bromomethylstyrene*, $C_{10}H_7OBr_4I$, long, glistening prisms, m. p. 119°; the *methyl ether* of the former compound,

$$C_{12}H_{12}O_2Br_4,$$

crystallises in plates, m. p. 89°, and is converted (1) by cold concentrated sulphuric acid into 4 : 6-dibromo-5-methyl-2-methylenecoumaranone, *αβ*-3 : 5-*tetrabromo*-2-*methoxy*-*α*-p-*tolylpropionic acid*, $OMe\cdot C_6HMeBr_2\cdot CBr(CH_2Br)\cdot CO_2H$, small, slender, white needles, m. p. 235°, and *β* : *β* : 3 : 5-*tetrabromo*-2-*methoxy*-4-*methyl*-*α*-*bromomethylstyrene*, $OMe\cdot C_6HMeBr_2\cdot C(CH_2Br):CBr_2$, small, colourless plates, m. p. 123°; (2) by dilute nitric acid into 3 : 5-*dibromo*-2-*methoxy*-4-*toluic acid*, $C_9H_8O_3Br_2$, needles, m. p. 196°, the *methyl* ester of which, $C_{10}H_{10}O_3Br_2$, forms prisms, m. p. 55°.

[With P. Moskopp.]—4-*Hydroxy*-m-*cymene*, $C_{10}H_{14}O$, is prepared by reducing 2-hydroxy-*α* : 5-dimethylstyrene with sodium and alcohol; it crystallises in slender needles, m. p. 35°, b. p. 227°/750 mm.; the *benzoate*, $C_{17}H_{18}O_2$, forms large prisms, m. p. 60°.

α : *β* : 5-*Tetrabromo*-4-*hydroxy*-1-*methyl*-*α*-*bromomethyl*-3-*ethylbenzene*, $OH\cdot C_6H_2MeBr\cdot CBr(CH_2Br)\cdot CHBr_2$, prepared by acting on 2-hydroxy-*α* : 5-dimethylstyrene or the hydroxy-*m*-cymene just described with bromine in chloroform, forms stellate aggregates of compact, glistening needles, m. p. 131°; the *acetate*, $C_{12}H_{11}O_2Br_5$, forms white, glistening crystals, m. p. 136°. The former compound is converted (1) by zinc and hydrochloric acid into 5-*bromo*-6-*hydroxy*-*α* : 3-*dimethylstyrene*, $C_{10}H_{11}OBr$, an oil, b. p. 129—134°/15 mm.; (2) by aqueous acetone into *β* : *β* : 5-*tribromo*-6-*hydroxy*-3-*methyl*-*α*-*bromomethylstyrene*, $C_{10}H_8OBr_4$, which crystallises in glistening, white plates, m. p. 101°, yields an *acetate*, $C_{12}H_{10}O_2Br_4$, plates, m. p. 95°, and is converted by alkali into 1 : 6-*dibromo*-4-*methyl*-2-*bromomethylcoumarone*,

$$C_6H_2MeBr\begin{<}C(CH_2Br)\\ \text{---}O\text{---}\end{>}CBr,$$

white needles, m. p. 128°; (3) by methyl alcohol at 100° into *β* : 5-*dibromo*-6-*hydroxy*-*β*-*methoxy*-3-*methyl*-*α*-*bromomethylstyrene*,

$$C_{11}H_{11}O_2Br_3,$$

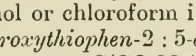
which crystallises in slender, white needles, m. p. 135°, forms an *acetate*, white cubes, m. p. 66°, and, when acted on by hydrogen iodide in glacial acetic acid, yields *β* : 5-*dibromo*-*β*-*iodo*-6-*hydroxy*-3-*methyl*-*α*-*bromomethylstyrene*, $OH\cdot C_6H_2MeBr\cdot C(CH_2Br):CBrI$, glistening prisms, m. p. 115°; and (4) by ethyl alcohol into the corresponding *ethoxy*-compound, $C_{12}H_{13}O_2Br_3$, small plates, m. p. 68°. W. H. G.

Synthetical Experiments with Esters of Thiodiglycollic Acid. Oscar Hinsberg (*Ber.*, 1910, **43**, 901—906).—In ethyl thiodiglycollate, $S\cdot(CH_2\cdot CO_2Et)_2$, both methylene groups are placed between two negative groups. They are found to be strongly negative, and very readily react with *α*-dicarbonyl compounds: for example, *o*-diketones, *o*-quinones, *o*-keto-esters, and oxalic acid esters. As the *α*-carbethoxy-group has only a relatively faint activating influence, the *α*-sulphur atom is proved to belong also to the activating atomic groups.

Ethyl thiodiglycollate reacts with benzil in presence of sodium, forming a product which, after hydrolysis of the ester, crystallises in colourless, glistening needles. The 3:4-*diphenylthiophen*-2:5-*dicarboxylic acid* formed decomposes at 300° when heated, forming 3:4-diphenylthiophen.

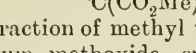
Phenanthraisothiophendicarboxylic acid (annexed constitution), prepared in a similar manner from phenanthraquinone, crystallises in minute, yellow needles, decomp. 270°, whereby *phenanthraisothiophen* is formed; this separates from alcohol or chloroform in light yellow plates, m. p. 163°.

Methyl 3:4-*dihydroxythiophen*-2:5-*dicarboxylate*,

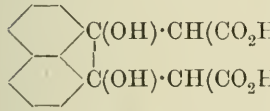


prepared by the interaction of methyl thiodiglycollate and ethyl oxalate in presence of sodium methoxide, crystallises in colourless needles, m. p. 178°. The alkali salts are bright yellow. In alcoholic solution the ester gives a blue coloration with ferric chloride, changing to red on the addition of sodium carbonate. The ester is hydrolysed with difficulty. The corresponding *ethyl* ester forms colourless needles, m. p. 134°.

Ethyl hydrogen 3-*hydroxy*-4-*methylthiophen*-2:5-*dicarboxylate*,



prepared by the interaction of ethyl thiodiglycollate, ethyl pyruvate, and sodium methoxide, crystallises from dilute alcohol in colourless needles, m. p. 233°. When boiled with dilute sodium hydroxide, 3-*hydroxy*-4-*methylthiophen*-5-*carboxylic acid* is obtained in very slender, long needles, m. p. 184°.



Dihydroxytetrahydroacenaphthaisothiophendicarboxylic acid (annexed constitution), obtained by the interaction of ethyl thiodiglycollate and acenaphthenequinone, forms small, colourless needles, decomp. 250°.

E. F. A.

Gnoscopine (*r*-Narcotine). Paul Rabe and Andrew McMillan (*Ber.*, 1910, **43**, 800—804. Compare Abstr., 1907, i, 790; W. H. Perkin and Robinson, Proc., 1910, **26**, 46).—The properties and reactions of gnoscopine all point to the conclusion that it is *r*-narcotine. It is obtained by heating narcotine with absolute alcohol at 175° for six hours, or with dilute alcohol in a reflux apparatus during eight days. The *hydrochloride*, $C_{22}H_{23}O_7N,HCl$, crystallises in colourless needles, has m. p. 238° (decomp.), and is hydrolysed by water. The *picrate* has m. p. 185°, and the *picrolonate*, 232° (decomp.). When oxidised with nitric acid, both narcotine and gnoscopine yield cotarnine, and when heated with water at 140°, both alkaloids yield hydrocotarnine.

It has been found possible to resolve gnoscopine methiodide by means of silver bromocamphorsulphonate.

Narcotine methyl bromocamphorsulphonate, $C_{33}H_{40}O_{11}NBrS$, crystallises in colourless needles, has m. p. 231° (decomp.), and $[\alpha]_D^{23}$ +101°. J. J. S.

Conversion of Guanine into Xanthine by means of Hydrochloric Acid. Emil Fischer (*Ber.*, 1910, **43**, 805—806).—Guanine (1 gram) gives a 60—70% yield of xanthine when heated with 100 c.c. of 25% hydrochloric acid for thirty-two hours in a reflux apparatus.

The decomposition is analogous to the formation of dialkylmalonylcarbamides and ammonia from dialkylmalonylguanidines. J. J. S.

Behaviour of Histidine towards Picrolonic Acid. P. Brigl (*Zeitsch. physiol. Chem.*, 1910, **64**, 337—340).—Histidine and picrolonic acid yield the yellow monopicrolonate, $C_6H_9O_2N_3,C_{10}H_8O_5N_4$, whereas the mono- and di-hydrochloride of the base yield the orange dipicrolonate, $C_6H_9O_2N_3,2C_{10}H_8O_5N_4$, even when only one gram-molecule of picrolonic acid is used. The yields when the hydrochlorides are made use of are poor, and the method cannot be employed for estimating histidine. The dipicrolonate can also be prepared from the free base if an excess of picrolonic acid is used. J. J. S.

Derivatives of Histidine. Hermann Pauly (*Zeitsch. physiol. Chem.*, 1910, **64**, 75—81).—p-*Nitrobenzoylhistidine*,

$$C_6H_8N_3O_2\cdot CO\cdot C_6H_4\cdot NO_2,$$

prepared by adding a benzene solution of *p*-nitrobenzoyl chloride and an aqueous solution of sodium hydroxide to a well-stirred ice-cold aqueous solution of histidine hydrochloride, crystallises in slender needles, m. p. 251—252°. In the preparation of histidine anhydride from histidine methyl ester (Fischer and Suzuki, Abstr., 1905, i, 121; 1906, i, 73), in addition to the *l*-anhydride a certain amount of the less soluble *d-l*-anhydride is formed. The *l*-anhydride has m. p. 328° in a closed evacuated tube; it crystallises with $2\frac{1}{2}H_2O$, which it loses at 140°. Its solution in *N*-hydrochloric acid has $[\alpha]_D^{20}$ −66·24°. The anhydride yields insoluble *silver*, $C_{12}H_{12}O_2N_6Ag_2$, and *mercuric* salts.

d-l-*Histidine anhydride* has also m. p. 328°. A better yield of the racemic anhydride is obtained when histidine ethyl ester is heated to 160° for several hours. J. J. S.

Synthesis of Hordenine. Eugène Léger (*Bull. Soc. chim.*, 1910, [iv], **7**, 172—173. Compare Abstr., 1906, i, 204, 761).—A claim for priority over Barger (Trans., 1909, **95**, 2193). W. O. W.

Constants of the First and Second Dissociations of Quinine. J. O. Wakelin Barratt (*Zeitsch. Elektrochem.*, 1910, **16**, 130—132).—The concentration of the hydroxyl ions in a solution of quinine was measured by adding phenolphthalein to it, and then mixing solutions of disodium hydrogen phosphate and trisodium phosphate with phenolphthalein until the same colour was obtained. Salm's determinations of the acidity of these solutions were used

(Abstr., 1904, ii, 536, and *Zeitsch. physikal Chem.*, 1906, 57, 471). From these data the first dissociation constant is found to be $2{\cdot}6 \times 10^{-6}$ at 16—18°.

The second constant is obtained by measuring the hydrolysis of quinine dihydrochloride (also by Salm's method, using methyl-orange and hydrochloric acid for comparison). It is $1{\cdot}3 \times 10^{-10}$ at 16—18°.

T. E.

[Preparation of Dioxindols.] Kalle & Co. (D.R.-P. 217556. Compare this vol., i, 278).—Condensation products from dioxindole and 3-oxy-(1)-thionaphthen have previously been described; it is now found that the alkyloxy-dioxindoles of the general formula

$$OR{\cdot}C_6H_3{<}\begin{matrix}CH(OH)\\ NH\end{matrix}{>}CO, \quad R = \text{alkyl},$$

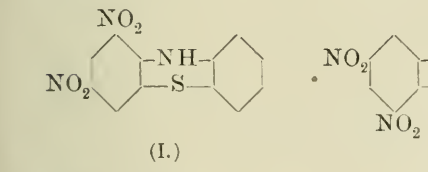
also react in this condensation, yielding brown to yellow dyes.

7-Methoxyisatin is reduced to the corresponding 4-methoxy-dioxindole, and this on condensation with 3-oxy-(1)-thionaphthen yields a brown powder, whilst with 6-ethoxy-3-oxy-(1)-thionaphthen-2-carboxylic acid a yellow dye is formed. F. M. G. M.

Preparation of β-Naphthindoxyl. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 216639).—When compounds of the type β-$C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}CO_2R$, where R is hydrogen, alkyl or aryl groups, are heated at 100—110° with acid condensation agents, such as aluminium chloride or phosphoric oxide, β-naphthindoxyls are produced, which, on atmospheric oxidation in alkaline solution, are converted into β-naphthylindigotin.

β-Naphthindoxyl, an olive-green powder when freshly-prepared, is readily soluble in organic solvents, from which it separates in greenish-yellow needles, m. p. 80—85°. F. M. G. M.

Thiazines. R. Mitsugi, Heinrich Beyschlag, and Richard Möhlau (*Ber.*, 1910, 43, 927—934).—Kehrmann (Abstr., 1900, i, 61) has ascribed the formula (I) to the dinitrophenthiazine obtained from *o*-aminothiophenol hydrochloride by the action of picryl chloride in presence of sodium acetate. The authors now assign the formula (II) to this compound. It is considered that the chlorine atom of picryl chloride attacks, not the amino-group, but the sulphydryl group of *o*-aminothiophenol.



(I.) (II.)

When molecular proportions of dibenzoyl-*m*-diamino-*m*-thiocresol and picryl chloride interact, *trinitrophenyl dibenzoyldiaminotolyl sulphide*, $C_6H_2Me(NHBz)_2{\cdot}S{\cdot}C_6H_2(NO_2)_3$, is formed. This separates in orange-yellow crystals, m. p. 234° (decomp.). It dissolves in alcoholic sodium hydroxide in the cold with a blood-red coloration, forming *dinitrodibenzoylaminophenotoluthiazine*,

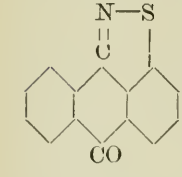
$$C_6H_2Me(NHBz){<}\begin{matrix}NBz\\ S\end{matrix}{>}C_6H_2(NO_2)_2,$$

which separates from acetic acid in brownish-yellow, glistening plates. On boiling with alcoholic sodium hydroxide, the benzoyl group attached to the nitrogen atom of the thiazine ring is eliminated, and *dinitrobenzoylaminophenotoluthiazine* is formed, crystallising in deep blackish-violet, glistening prisms.

On reduction with stannous chloride, *diaminobenzoylaminophenotoluthiazine*, $C_6H_2Me(NHBz)<^{NH}_{S}>C_6H_2(NH_2)_2$, is formed. The *stannichloride* forms concentrically-grouped, long needles. On oxidation, it is converted into *diaminobenzoylaminophenotoluazothionium chloride*. The *ferrichloride*, $C_{20}H_{17}ON_4SCl,FeCl_3 + H_2O$, separates in lustrous, deep blackish-violet prisms. It dissolves in alcohol with an olive-yellow coloration, and forms an almost insoluble *platinichloride* and *dichromate*. The *diacetate* forms faintly yellow-coloured, long needles, and in presence of aniline it is converted by ferric chloride into *7-benzoylamino-2 : 4-diacetyldiamino-3-anilinophentoluazothionium 6-chloride*, $C_6H_2Me(NHBz)<^{N}_{SCl}>C_6H(NHAc)_2\cdot NHPh$, which is a black, crystalline powder. When boiled with hydrochloric acid, *2 : 4-diamino-7-benzoylamino-3-anilinophenotoluazothionium 6-chloride*, a bluish-black, crystalline powder, is obtained. E. F. A.

Preparation of Sulphur and Nitrogen Derivatives of Anthraquinone. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 216306; 217688).—When anthraquinone-*a*-mercaptans are heated with aqueous ammonium hydroxide in the presence of sulphur at 100°, anthrathiazoles are obtained.

1-*Anthrathiazole* (annexed formula) crystallises from pyridine in prisms. 4-*Amino*-1-*anthrathiazole*, prepared from 4-amino-1-anthraquinone mercaptan, separates from the same solvent in yellow leaflets; it can also be obtained from 4-*amino*-1 *thiocyanoanthraquinone*, a brownish-red powder.



1-*Thiocyano*-2-*methylanthraquinone*, a yellowish-brown powder, yields 2-*methyl*-1-*anthrathiazole*, golden-yellow needles sparingly soluble in alcohol.

1 : 4-*Dithiocyanoanthraquinone*, yellowish-brown crystals (obtained from 4-chloro- or 4-nitro-1-diazoanthraquinone), yields 1-*anthrathiazole* 4-*mercaptan*, yellow needles soluble in alcohol.

1 : 5-Anthradithiazole, yellow needles, is prepared from potassium anthraquinone-1 : 5-disulphonate.

5-*Amino*-1-*anthrathiazole*, reddish-brown prisms, is obtained from sodium 5-aminoanthraquinone-1-sulphonate.

The condensation and reduction of sodium 1-chloro-4-nitroanthraquinone-8-sulphonate yields 4-*amino*-1-*anthrathiazole*-8-*sulphonic acid*.

These substances all give characteristic colour reactions with concentrated sulphuric acid, sodium hydroxide, and formaldehyde, which are tabulated in the patent.

In the second patent (217688) it is stated that the presence of free sulphur is not necessary for the preparation of anthrathiazoles.

1-Anthrathiazole can be prepared by heating α-thiocyanoanthraquinone with ammonia at 140° under pressure:

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3\cdot SCN + NH_3 = \begin{matrix}C_6H_4\cdot C{=\!=}N\\ |\quad\quad |\\ CO{-\!-}C_6H_3\cdot S\end{matrix} + HCN + H_2O.$$

F. M. G. M.

Displaceability of the Nitro-group. Giacomo Ponzio (*Atti R. Accad. Sci. Torino*, 1910, **45**, 191—196).—The ease with which a nitro-group occurring in an aromatic compound in the ortho-position to another negative group can be displaced by an amino- or anilino-group finds an analogy in the readiness with which an amino- or anilino-group can be substituted for the ω-nitro-group of the ω-nitrobenzaldehydenitrophenylhydrazones (compare this vol., i, 192). Thus, with ammonia, the compound $NO_2\cdot CR{:}N_2H\cdot Ar\cdot NO_2$ gives

$$NH_2\cdot CR{:}N_2H\cdot Ar\cdot NO_2,$$

and with aniline, $NHPh\cdot CR{:}N_2H\cdot Ar\cdot NO_2$. The position of the nitro-group in the benzene nucleus of the phenylhydrazine residue has very little influence on these reactions, *o*-nitrophenylhydrazones reacting only slightly more slowly than the corresponding para-derivatives. The presence of a nitro-group in the phenylhydrazine residue is, however, a necessary condition for the above substitution of the ω-nitro-group, neither ω-nitrobenzaldehydephenylhydrazone nor ω : *m*-dinitrobenzaldehydephenylhydrazone being capable of reacting with alcoholic ammonia.

The analogy breaks down when the behaviour of these two classes of nitro-compounds towards sodium hydroxide or alkyloxide is considered. Thus, 1 : 2-dinitrobenzene with sodium hydroxide or methoxide gives *o*-nitrophenol or *o*-nitroanisole, whilst, under the same conditions, ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone gives always α-dinitrotetraphenyltetrazoline (*loc. cit.*).

ω-*Anilinobenzaldehyde*-p-*nitrophenylhydrazone*,

$$NHPh\cdot CPh{:}N_2H\cdot C_6H_4\cdot NO_2,$$

forms brown needles with a green reflex, m. p. 180—181°.

ω-*Anilinobenzaldehyde*-o-*chloro*-p-*nitrophenylhydrazone*,

$$NHPh\cdot CPh{:}N_2H\cdot C_6H_3Cl\cdot NO_2,$$

forms red needles, m. p. 162°. T. H. P.

Indigotin. IV. Brominated Indigotins. Eugène Grandmougin (*Ber.*, 1910, **43**, 937—941. Compare this vol., i, 73, 74).—When indigotin is brominated, the halogen enters first positions 5 and 5′, then 7 and 7′, and finally 4 and 4′. 4 : 5 : 7 : 5′ : 7′-*Pentabrómoindigotin*, obtained by treating indigotin with an excess of bromine in the presence of concentrated sulphuric acid, separates from boiling xylene, pyridine, or nitrobenzene in microscopic needles. By oxidation by chromic and acetic acids, it yields a mixture of di- and tri-bromoisatin, from which, after distillation with potassium hydroxide and acetylation of the resulting bromoanilines, 2 : 4 : 5-tribromoacetanilide and 2 : 4-dibromoacetanilide are derived. 4 : 5 : 7 : 4′ : 5′ : 7′-*Hexabromoindigotin*, obtained by bromination in chlorosulphonic acid, separates from boiling nitrobenzene in dark blue needles, and forms a green

solution in concentrated sulphuric acid. 4 : 5 : 7-*Tribromoisatin*, m. p. 257—258°, obtained from it by oxidation with fuming nitric and acetic acids, forms orange crystals, develops an intense violet coloration with alkali hydroxides, and yields 2 : 4 : 5-tribromoaniline by distillation with potassium hydroxide. C. S.

Preparation of Dehydroindigotin, its Homologues, and Substitution Products. Ludwig Kalb (D.R.-P. 216889).—The preparation of dehydroindigotin and its dibromo-derivative has been previously described (Abstr., 1909, i, 966). The author has now prepared *dimethyldehydroindigotin* in a similar manner from dimethylindigotin; it forms yellowish-brown tablets, m. p. 155—160° (decomp.). F. M. G. M.

Preparation of 1-*p*-Dialkylaminophenyl-2-alkyl-3-hydroxymethyl-5-pyrazolones. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 217557 and 217558. Compare this vol., i, 78).—When 1-*p*-aminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone is treated in aqueous solution with chloroacetic acid and the mixture acidified, 1-p-*aminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethylpyrazolonedi*-ω-*acetic acid* is precipitated as a crystalline powder, which when heated at 235° evolves carbon dioxide, or with dilute hydrochloric acid at 140—150° during ten to twelve hours yields 1-*p*-dimethylaminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone.

1-p-*Cyanomethylaminophenyl*-2:4-*dimethyl*-3-*hydroxymethylpyrazolone*, an oil, is prepared by treating 1-*p*-aminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone with aqueous formaldehyde, sodium hydrogen sulphite, and subsequently warming with potassium cyanide; on methylation it yields 1-p-*methyl*-ω-*cyanomethylaminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone*, which undergoes hydrolysis with dilute sulphuric acid.

1-p-*Dimethylaminophenyl*-2-*methyl*-3-*hydroxymethyl*-5-*pyrazolone*, m. p. 186°, is obtained by heating 1-*p*-aminophenyl-2-methyl-3-hydroxymethyl-5-pyrazolone with methyl iodide in methyl-alcoholic solution during six to eight hours; it forms colourless crystals, readily soluble in hot, sparingly so in cold water.

The condensation of *p*-nitrophenylhydrazine with ethoxyacetylmalonic ester yields *ethyl* 1-p-*nitrophenyl*-3-*ethoxymethyl* 5-*pyrazolone*-4-*carboxylate*, yellow crystals, m. p. 135—137°, which on heating with hydrochloric acid loses ethyl alcohol and carbon dioxide, giving 1-p-*nitrophenyl*-3-*hydroxymethyl*-5-*pyrazolone*; this on methylation forms 1-p-*nitrophenyl*-2-*methyl*-3-*hydroxymethyl*-5-*pyrazolone*, and on subsequent reduction yields 1-p-*aminophenyl*-2-*methyl*-3-*hydroxymethyl*-5-*pyrazolone*, m. p. 223—225°.

The condensation of *p*-nitrophenylhydrazine with ethyl acetoacetate gives 1-p-*nitrophenyl*-3-*methyl*-4-*ethyl*-5-*pyrazolone*; this on methylation forms 1-p-*nitrophenyl*-2 : 3-*dimethyl*-4-*ethyl*-5-*pyrazolone*, yellow crystals, m. p. 129—131°, which on bromination yields 1-p-*nitrophenyl*-2-*methyl*-3-*bromomethyl*-4-*ethyl*-5-*pyrazolone*, crystallising in yellow crystals, m. p. 163—165°. The foregoing bromo-compound when heated at 120° in water gives 1-p-*nitrophenyl*-2-*methyl*-3-*hydroxymethyl*-4-*ethyl*-5-

pyrazolone, m. p. 169—170°, which when reduced yields 1-p-*aminophenyl*-2-*methyl*-3-*hydroxymethyl*-4-*ethyl*-5-*pyrazolone*, a crystalline powder, m. p. 244—245°; this on methylation is converted into 1-p-*dimethylaminophenyl*-2-*methyl*-3-*hydroxymethyl*-4-*ethyl*-5-*pyrazolone*, m. p. 183—184°. F. M. G. M.

Application of Physico-chemical Methods to Determine the Mechanism of Organic Reactions. Arthur Michael (*Amer. Chem. J.*, 1910, 43, 322—358).—Acree (Abstr., 1907, i, 258), in the course of a study of the behaviour of the metallic salts of tautomeric compounds, discussed the theories advanced by Comstock, Wheeler, Nef and Michael, gave reasons for considering them inadequate to account for the observed reactions, and stated the following generalisation. "A salt of a tautomeric compound reacts with an alkyl halide or other reagent, and forms two compounds, because the tautomeric salt is really a mixture of two tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions." He has also stated (Abstr., 1908, i, 920) that when solutions of the salts of 1-phenyl-4-methylurazole are treated with alkyl halides, the latter react with the enolic and ketonic anions of the salts.

In the present paper, these conclusions are criticised at considerable length. It is stated that Acree's interpretations of the mechanism of tautomeric reactions are untenable, and that the results which he obtained in the alkylation of urazole derivatives show that these reactions proceed in accordance with the law of mass action and furnish evidence in support of the "addition theory."

The author protests against theories being put forward with regard to the mechanism of organic reactions which are based on results obtained by physico-chemical methods adapted to the study of dilute solutions of inorganic electrolytes, when the results obtained in other ways and the chemical aspects of the problems are ignored.

E. G.

Urazoles. XV. Reactions of Diazoalkyls with 1-Phenyl-2-methylurazole. Sidney Nirdlinger and Salomon F. Acree (*Amer. Chem. J.*, 1910, 43, 358—384).—In previous papers (Abstr., 1908, i, 919; 1908, ii, 163) the tautomeric behaviour of phenylurazole and its derivatives has been studied with particular reference to the reactions of their metallic salts.

In the present paper, an account is given of the reactions of the urazoles with diazo-derivatives of methane, ethane, propane, butane, and propylene. These substances were selected for study, since they all, except the last, react very rapidly with the urazoles, and yield a mixture of isomeric *O*- and *N*-esters which can be quantitatively separated. It has been found that the equilibrium constants of urazole salts differ from those of the urazoles themselves, but the differences cannot be measured by conductivity methods. A discussion is given of the conditions affecting the constant ratio of products obtained from a tautomeric substance.

1-Phenyl-2-methylurazole, when alkylated with different proportions of diazo-hydrocarbons under similar conditions, yields a constant ratio of esters, thus showing that the constants for the velocity of

rearrangement of the two forms of the compound are very large in comparison with K_{trans} and K'_{trans}, the velocity constants of the reactions of the ketonic and enolic forms respectively with the diazo-compound, or, in other words, that K_3, the equilibrium ratio between the molecular enolic and ketonic forms, is maintained constant during the alkylation. In different solvents, the reaction between 1-phenyl-2-methylurazole and a given diazo-hydrocarbon yields different ratios of the *O*- and *N*-esters; in the same solvent, the urazole and different diazo-compounds give different ratios of esters.

1-Phenyl-2-methylurazole, when treated with diazomethane or diazoethane in presence of its sodium derivative, gives different ratios of esters from those obtained when the sodium salt is absent, and hence the conclusion is drawn that the equilibrium point of the two tautomeric forms of the sodium salt may be different from that of the two forms of the urazole itself, and thus afford an explanation of abnormal hydrolysis.

[With Wm. J. Heaps.]—1-*Phenyl*-2-*methyl*-4-*ethylurazole*, m. p. 112°, obtained by the action of methyl iodide on 1-phenyl-2-methylurazole in presence of potassium hydroxide, evaporating the product to dryness, and treating the residue with hydrochloric acid in order to hydrolyse any *O*-ester present, is a white solid. The corresponding 4-*propyl* and 4-iso*amyl* derivatives have m. p. 75° and 179° respectively; the 4-*butyl* derivative was obtained as a heavy oil.

Propylurethane, b. p. 191·5—192·5°/758 mm., obtained by the action of ethyl chlorocarbonate on propylamine, is a colourless liquid; its *nitroso*-derivative, b. p. 94°(uncorr.)/35 mm., is a red oil. *Butylurethane* has b. p. 208—211°(uncorr.)/770 mm.; its *nitroso*-derivative is a viscous oil. *Allylurethane* has b. p. 194·5—195°(uncorr.)/768 mm.; its *nitroso*-derivative was obtained as a red oil.

1-Phenyl-2-methyl-4-allylurazole, m. p. 61—64°, can be obtained either by the action of diazopropylene on 1-phenyl-2-methylurazole or by the action of allyl iodide on the sodium derivative. E. G.

Condensation of Azoimide with Fulminic Acid. I. F. Carlo Palazzo (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 218—222).—The interaction of azoimide and fulminic acid yields, not triazoformoxime, $N_3{\cdot}CH{:}NOH$, but a compound exhibiting all the characters of a 1-hydroxytetrazole. The reaction is probably expressed by the following scheme:

$$C{:}N{\cdot}OH + N_3H = N_3{\cdot}CH{:}NOH \longrightarrow N\lessdot^{N{\cdot}N{\cdot}OH}_{N{:}CH}$$

(compare Thiele, Abstr., 1892, 1298; Hantzsch and Vagt, Abstr., 1901, i, 194; Forster, Trans., 1909, **95**, 184; Schroeter, Abstr., 1909, i, 773).

1-*Hydroxytetrazole*, CH_2ON_4, forms slender, acicular crystals, m. p. 145° (decomp. with deflagration), and, like most compounds containing the group $:N{\cdot}OH$ in a heterocyclic chain (compare Peratoner, Abstr., 1902, i, 493), gives with ferric chloride a faint red coloration tending towards brown. The behaviour of 1-hydroxytetrazole towards alkalis corresponds completely with that exhibited by 1-hydroxy-5-phenyltetrazole (compare Forster, *loc. cit.*); gentle heating with 25—30%

alkali solution results in the liberation of one-half of the nitrogen as such, whilst the other half, including the hydroxyiminic nitrogen, is eliminated as ammonia. Similar proportions of nitrogen and ammonia are obtained on heating the compound with concentrated hydrochloric acid in a sealed tube, the hydroxyiminic group here being reduced by the formic acid, which is itself oxidised to carbon dioxide. Among the products of decomposition by concentrated sulphuric acid at a moderately low temperature, hydroxylamine is found.

T. H. P.

Action of Azoimide on Methylcarbylamine: Synthesis of Homologues of Tetrazole. E. Oliveri-Mandalà (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 228—231).—On treating an ethereal solution of anhydrous azoimide with methylcarbylamine, a compound is obtained which gives analytical numbers corresponding with an additive compound of the two substances, but which cannot be regarded as such, as it is not decomposed by prolonged boiling with water, but, like tetrazole, is decomposed completely by alkali into carbon dioxide, methylamine, ammonia, and nitrogen. An additive compound is probably formed first, the reactivity of the triazo-group then causing an immediate intramolecular condensation with formation of the heterocyclic tetrazole ring:

$$N_3{\cdot}CH{:}NMe \longrightarrow N\!\!<\!\!\begin{matrix} N{:}CH \\ | \\ N{\cdot}NMe \end{matrix}$$

(compare Forster, Trans., 1909, **95**, 184; Schroeter, Abstr., 1909, i, 773).

The *compound*, $C_2H_4N_4$, thus obtained forms hard, elongated prisms with quadrilateral bases, m. p. 36—37°, and exhibits normal cryoscopic behaviour in benzene. Decomposition with boiling concentrated alkali solution takes place according to the equation:

$$C_2H_4N_4 + 2H_2O = N_2 + NH_2Me + NH_3 + CO_2.$$

T. H. P.

Albumin from the Serum of Horse's Blood Deposited on Dialysis into Water. Stephan Maximowitsch (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 330—337. Compare Abstr., 1902, i, 66; 1906, i, 224).—Defibrinated horse's blood was mixed with an equal volume of saturated ammonium sulphate solution and the precipitate filtered, washed with semi-saturated ammonium sulphate solution, dissolved in water, and again precipitated and washed. The precipitate was then dialysed, the solution formed in the dialyser gradually depositing a precipitate as the salts present were removed. This precipitated protein, and that remaining in solution in the dialyser have the following compositions: C, 52·76, 52·61; H, 6·90, 6·83; N, 15·63, 15·53; S, 1·200, 1·211; $[\alpha]_D$ −50·20°, −50·63°. Similar close agreement is observed between the properties of the two derivatives formed with hydrogen chloride. Both parts of this globulin precipitate are therefore apparently identical. Their different behaviour with reference to water is probably due to the presence in the serum of some substance which prevents part of the globulin from

dissolving, and is gradually removed on dialysis, so that the insoluble portion slowly becomes soluble. T. H. P.

The Relations of Proteins to Crystalloids. II. The Osmotic Pressure of Ionising Salts of Serum Proteins. Herbert E. Roaf (*Quart. J. exp. Physiol.*, 1910, 3, 171—184. Compare this vol., i, 209).—Observations on amino-acids and proteins confirm the view that these substances form salts with acids and alkali which are ionised, and behave like the salts of fairly strong bases and acids. The formation of such salts is possible in the body, and may explain certain physiological phenomena. W. D. H.

Changes in the Physical Conditions of Colloids. IX. Wolfgang Pauli and Hans Handovsky (*Biochem. Zeitsch.*, 1910, 24, 239—262).—Dialysed serum solutions lose, after addition of alkali, their coagulability, which can be restored by addition of salts. The authors have investigated quantitatively the amounts of salts necessary to restore this coagulability in the presence of varying quantities of alkali. They show that the salts of alkaline earths react in this respect more powerfully than those of the alkali metals. They have also determined the coagulation temperatures of the alkaline protein solutions in the presence of various salts, and some of the results are plotted in the form of curves. They have also determined the viscosities and electrical conductivities of some of the mixtures, and have shown that the addition of salts decreases the viscosity of the alkaline protein solution. In these respects, again, the salts of alkaline earths have a more pronounced action than those of the alkali metals. They give formulæ to explain the various phenomena, assuming that on addition of salts the number of hydrated particles of alkali protein is diminished. S. B. S.

Salts of Cytosine, Thymine, and Uracil. Victor C. Myers (*J. Biol. Chem.*, 1910, 7, 249—258).—The following thymine salts are described: *Sodium*, $C_5H_5O_2N_2Na$, long needles; potassium, $C_5H_5O_2N_2K,\frac{1}{2}H_2O$, small needles; *mercuric*, $C_5H_4O_2N_2Hg$, and *lead*, $C_5H_4O_2N_2Pb,2H_2O$, short needles. Uracil also yields metallic salts; the following have been prepared (compare Johnson and Clapp, Abstr., 1908, i, 836): *Sodium*, $C_4H_3O_2N_2Na,\frac{1}{2}H_2O$; *potassium*, $C_4H_3O_2N_2K,H_2O$; *mercuric*, $C_4H_2O_2N_2Hg$, and *lead*, $C_4H_2O_2N_2Pb$.

The sodium salts of both thymine and uracil are convenient for physiological work on account of their solubility, and the comparative insolubility of the two mercuric salts, especially in alkaline solution, can be made use of in precipitating the compounds. The two *silver* salts form gelatinous precipitates which cannot be purified readily. J. J. S.

The Uric Acid Combinations with Nucleic Acid. Alfred Schittenhelm (*Chem. Zentr.*, 1910, i, 36; from *Zeitsch. expt. Path. Ther.*, 1909, 7, 110—115).—The compound formed from one molecular equivalent of nucleic acid and two of uric acid, and isolated in the

form of a copper salt by Y. Seo, does not, according to the author, exist, and is only a mixture, the composition of which can be varied by preparing it from varying quantities of the nucleic and uric acids.

S. B. S.

The Presence of Iron in True Nucleic Acids. F. Sauerland (*Zeitsch. physiol. Chem.*, 1910, 64, 16—20).—Nucleic acid from calves' thymus and nucleic acid from herring's spermatozoa contain the merest traces of iron; some samples contain none, others 0·02% to 0·03%. The conclusion is drawn that pure nucleic acid does not contain iron. As most nucleo-proteins contain iron, the question arises as to the part of the molecule in which the iron is to be found. The author suggests that the iron in the nucleo-proteins is due to the presence of impurities. This view is confirmed, as a pancreas nucleo-protein has been obtained practically free from iron (compare Hammarsten, Abstr., 1894, i, 310). J. J. S.

Formation of Proline by the Hydrolysis of Gelatin with Barium Hydroxide. Emil Fischer and Reginald Boehner (*Zeitsch. physiol. Chem.*, 1910, 65, 118—123).—Proline may either be a primary product of protein hydrolysis or be formed as a secondary product from α-amino-δ-hydroxyvaleric acid (Sörensen, Abstr., 1905, i, 749). Such change is not caused by heating with barium hydroxide. Gelatin, when hydrolysed by barium hydroxide, yields 7·6% proline, a quantity somewhat larger than that hitherto obtained by acid or enzyme hydrolysis (compare Fischer, Levene, and Aders, Abstr., 1902, i, 512). Proline is accordingly a primary product of hydrolysis.

E. F. A.

Filtration of Diastases. Maurice Holderer (*Compt. rend.*, 1910, 150, 790—792. Compare this vol., i, 212).—Pepsin, emulsin, and the catalase of pork resemble the enzymes already studied in the way in which their filtering power is affected by the alkalinity of the medium. Addition of a neutral salt to a solution of pepsin neutral to methyl-orange restores the power of passing through porcelain. An emulsin prepared from almonds, without employing the usual precipitation by alcohol, was found to pass through filters, whatever the reaction of the solution, provided that the vegetable caseins were first rendered insoluble by treatment with acetic acid. W. O. W.

Chemical Composition and Formation of Enzymes. Hans Euler and Beth af Ugglas (*Zeitsch. physiol. Chem.*, 1910, 65, 124—140).—Portions of invertase solutions were heated for a known time at temperatures above 50° and their hydrolytic activity compared with unheated portions of the same solution. The "inactivity constant" K_E is given by the equation $K_E = 1/t \log. K_0/K$. The temperature-coefficient of this "inactivity constant" rises to a maximum. Invertase is only slightly sensitive to hydrogen ions, but exceedingly sensitive to $-OH$-ions, and it is compared in this respect with the behaviour of α-glucose on mutarotation. The temperature-coefficient of the hydrolysis of sucrose by invertase is much smaller than that of

the acid hydrolysis. Possibly heating or the presence of hydroxyl ions converts invertase into an inactive form. E. F. A.

Action of Dibasic Alkali Phosphates on Tyrosinase. Jules Wolff (*Compt. rend.*, 1910, **150**, 477—479. Compare Abstr., 1909, i, 279).—Polemical against Agulhon (Thesis, 1910), who has stated that alkali dibasic phosphates have a retarding influence on the activity of tyrosinase. The author shows by experiments on tyrosine that, taking into consideration the formation of melanins, the extract of *Russula delica* is markedly activated by the addition of disodium phosphate. The melanins obtained in the absence of a phosphate are grey, those precipitated when this is present are deep black. W. O. W.

Halogenated *p*-Aminophenylarsinic Acids. Alfred Bertheim (*Ber.*, 1910, **43**, 529—536).—The arsenic acid group, which is so firmly bound in arsanilic acid and its homologues (Abstr., 1907, i, 812; 1908, i, 591; 1909, i, 75), is very easily eliminated by halogens from *p*-aminophenylarsinic acid, a solution of which in water or aqueous mineral acids yields an almost quantitative amount of tribromoaniline by treatment with bromine water. Mono- and di-halogenated arsanilic acids may be prepared, however, by the action of the halogen in an anhydrous solvent or in *statu nascendi*. Such acids are white, crystalline substances, less basic than arsanilic acid itself, and precipitated from aqueous solutions of their alkali salts by mineral acids. The monohalogenated acids are diazotised easily, the dihalogenated acids with some difficulty, yielding diazo-solutions of remarkable stability.

Bromoarsanilic acid, $NH_2 \cdot C_6H_3Br \cdot AsO(OH)_2$, is best prepared from arsanilic acid and bromine ($\frac{1}{2}$ mol.) in glacial acetic acid. *Iodoarsanilic acid* is prepared by the addition of mercuric oxide and iodine to a hot solution of arsanilic acid in methyl alcohol. *Dichloroarsanilic acid* is obtained by passing chlorine into a suspension of arsanilic acid in glacial acetic acid. *Dibromoarsanilic acid* is prepared by the slow addition of sodium hypobromite to a solution of arsanilic acid in dilute hydrochloric acid at 0°. *Di-iodoarsanilic acid* is obtained by adding arsanilic acid and then a solution of potassium iodide to a hot mixture of potassium iodate and dilute sulphuric acid. None of these acids undergo change below 250°. C. S.

Preparation of Salicylarsinic Acid (6-Hydroxy-1-carboxyphenyl-3-arsinic Acid). Wilhelm Adler (D.R.-P. 215251. Compare Abstr., 1908, i, 591).—The 6-hydroxy-1-carboxyphenyl-3-arsinic acid (salicylarsinic acid) prepared by Kahn and Benda (Abstr., 1909, i, 76) is found to be less toxic than *p*-aminophenylarsinic acid; its *barium* and *silver* salts are colourless, the *copper* salt, greenish-yellow, and the *iron* salt, brownish-red. F. M. G. M.

Isomeric Cinnamic Acids. III. Einar Biilmann [and, in part, Niels Bjerrum] (*Ber.*, 1910, **43**, 568—580. Compare Abstr., 1909, i, 155, 382; this vol., i, 174; Liebermann, Abstr., 1909, i, 303; this vol., i,

36, 175; Stoermer, *ibid.*, i, 115).—The three acids m. p. 42°, 58°, and 68° have practically the same dissociation constants, namely, $K \times 10^6 = 138$, 141, 142. The conclusion is drawn that all three acids yield solutions having the same electrical conductivity (compare Bader, Abstr., 1891, 257), and that the three acids are identical from the chemical point of view.

It has been shown previously (Abstr., 1902, i, 665) that the malenoid forms of olefine compounds containing two negative groups react with mercuric salts, yielding complex mercury compounds. As *allo*cinnamic acid reacts in this manner with mercuric chloride or acetate, whereas ordinary cinnamic does not, the conclusion is drawn that the *allo*-acid has the *cis*-configuration: $\begin{matrix}H\\Ph\end{matrix}\!\!>\!C{:}C\!<\!\!\begin{matrix}H\\CO_2H\end{matrix}$. The compound obtained is an *inner* salt of *α-mercuri-β-hydroxy-β-phenylpropionic acid*, $OH{\cdot}CHPh{\cdot}CH\!<\!\!\begin{matrix}CO_2\\|\\Hg\end{matrix}$, and is most readily prepared by the addition of a hot solution of mercuric acetate to a hot aqueous solution of *allo*cinnamic acid. It forms a colourless, microcrystalline precipitate with neutral properties, but dissolves in alkali solutions, yielding compounds of the type: $OH{\cdot}CHPh{\cdot}CH(Hg{\cdot}OH){\cdot}CO_2Na$. The alkaline solutions are not immediately precipitated by ammonium sulphide, but ultimately yield mercuric sulphide; the solutions react with acids, even carbonic acid, yielding precipitates which are richer in mercury than the original compound. The mercury compound reacts with potassium iodide solution according to the equation:

$$OH{\cdot}CHPh{\cdot}CH\!<\!\!\begin{matrix}CO_2\\|\\Hg\end{matrix} + 2KI + H_2O = OH{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2K + HgI_2 + KOH,$$

and when heated with hydrochloric acid, it yields mercuric chloride and ordinary cinnamic acid. In the latter reaction, β-hydroxy-β-phenylpropionic acid is undoubtedly formed as an intermediate product, but can be isolated more readily by the action of hydrogen sulphide on a solution of the mercury compound in dilute sodium hydroxide.

The complex mercury compounds derived from crotonic and maleic acids (Abstr., 1902, i, 665) are also decomposed by hydrogen sulphide in alkaline solution, yielding respectively β-hydroxybutyric acid and *dl*-malic acid.

The formation of these complex mercury compound appears to be a general method for (*a*) preparing β-hydroxy-acids from certain olefine acids, and (*b*) the elucidation of the *cis*- or *trans*-configuration of olefine acids. J. J. S.

Complex Mercury Compounds of Methyl Cinnamate and Cinnamic Acid. Walther Schrauth, Walter Schoeller, and Richard Struensee (*Ber.*, 1910, **43**, 695—699. Compare Biilmann, preceding abstract).—When methyl cinnamate is heated with a methyl-alcoholic solution of mercuric acetate at the ordinary temperature, a reaction occurs in which the alcohol participates, and *methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, $OMe{\cdot}CHPh{\cdot}CH(CO_2Me){\cdot}Hg{\cdot}OAc$, separates gradually in lance-shaped crystals, m. p. 140·5° (corr.). The

yield amounts to 65%. The acetoxy-group is very reactive, and is replaced by halogen when the substance is treated with halogen salts of sodium. The *chloride* has m. p. 133·5° (corr.); the *bromide*, m. p. 110·5°, and the *iodide*, m. p. 100°. The acetoxy-group is also replaced when the substance reacts with sodium diethylbarbiturate, the corresponding *veronal* derivative being formed. Saponification of methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate yields the internal *anhydride* of *α-hydroxymercuri-β-methoxy-β-phenylpropionic acid*, $CHPh(OMe)\cdot CH<\begin{matrix}CO_2\\ |\\ Hg\end{matrix}$, which decomposes at about 187° (corr.).

Methyl α-acetoxymercuri-β-ethoxy-β-phenylpropionate is prepared by the above method, ethyl alcohol being used instead of methyl alcohol; it has m. p. 123° (corr.). The corresponding *chloride* has m. p. 114°. On saponification the ester yields the internal *anhydride* of the corresponding *acid*. R. V. S.

Action of Dinitrophenylpyridinium Chloride on Mercuriated Amines. Fritz Reitzenstein and Georg Stamm (*J. pr. Chem.*, 1910, [ii], 81, 150—160).—Mercury derivatives of several compounds have been prepared to ascertain the influence of the metal on colour. *p*-Aminophenyl mercuriacetate reacts with dinitrophenylpyridinium chloride in boiling alcohol to form dinitroaniline and an insoluble, crystalline, brown *substance*, m. p. 244°, which probably has the constitution:

$$C_6H_4<\begin{matrix}N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot NH(HCl)\cdot C_6H_4\cdot Hg\cdot NH\cdot C_6H_3(NO_2)_2\\ Hg\cdot OAc\end{matrix}$$

(compare Zincke, Abstr., 1904, i, 921). The same two substances react in cold acetone to form an insoluble, brown, crystalline *substance*, $OAc\cdot Hg\cdot C_6H_4\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot NH(HCl)\cdot C_6H_4\cdot Hg\cdot OAc$, m. p. 164°. *p*-Aminophenyl mercuriacetate and dinitrophenylpyridinium chloride react in boiling alcohol to form an insoluble, reddish-brown *substance*,

$$HgCl\cdot C_6H_4\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot NH(HCl)\cdot C_6H_4\cdot Hg\cdot OH,$$

m. p. 125°, whilst in cold acetone a reddish-brown *substance*,

$$HgCl\cdot C_6H_4\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot NH(HCl)\cdot C_6H_4\cdot HgCl.$$

m. p. 151°, is produced. The insolubility of these four substances defeats the purpose of their preparation. 3-Mercury-*p*-toluidine, however, when dissolved in pyridine and heated with a methyl-alcoholic solution of dinitrophenylpyridinium chloride yields a brown *substance*, m. p. 133°, $\begin{matrix}CH{:}CH\cdot NH(HCl)\cdot C_6H_3Me\\ |\\ CH{:}CH\cdot CH{:}N\text{——}C_6H_3Me\end{matrix}>Hg$, which is soluble in chloroform. The solution is stated to exhibit faint absorption in the ultraviolet, whilst the analogous non-mercuriated substance prepared by Zincke (*loc. cit.*) shows absorption bands in the yellow and the green. C. S.

Organic Chemistry.

Chemical Effects of Ultraviolet Light on Gases. Polymerising Action. Daniel Berthelot and Henri Gaudechon (*Compt. rend.*, 1910, 150, 1169—1172).—Exposure of acetylene to the action of ultraviolet light brings about partial polymerisation of the gas, without decomposition and without formation of benzene. The product of polymerisation is a yellow solid, and the residual gas is pure acetylene. Under the same conditions, ethylene polymerises to a liquid having an odour of rancid fat, b. p. below 100°. The product resembles the mixture containing octylene, produced in the pyrogenic decomposition of waxes. Cyanogen is transformed into paracyanogen under the influence of ultraviolet light.

The presence of hydrogen or nitrogen with the acetylene does not modify the action, and mixtures of acetylene with ethylene or cyanogen give simple mixtures of the foregoing products.

W. O. W.

Action of Acetyl Halides on Unsaturated Hydrocarbons in the Presence of Aluminium Halides. S. Krapiwin (*Chem. Zentr.*, 1910, i, 1335—1336; from *Bull. Soc. Impér. Natur. Moscou*, 1908, 1).—Unsaturated ketones are obtained by the interaction of acetyl halides, unsaturated hydrocarbons, and aluminium halides, the best results being procured by intimately mixing the reacting substances in a solvent at a low temperature.

*cyclo*Propane (3 mols.), acetyl bromide (3 mols.), and aluminium bromide (4 mols.) in carbon disulphide yield a *ketone*, $C_3H_5\cdot COMe$, b. p. 103—104°/751 mm., D_4^{19} 0·8548, n_D 1·4253, which forms a *semicarbazone*, m. p. 169·5—170°; by the hydrolysis of the latter, a *ketone*, C_5H_8O, b. p. 96—97°/740 mm., D_4^{25} 0·8585, n_D 1·4240, is regenerated, which shows a marked tendency to polymerise, and forms a *semicarbazone*, m. p. 177—178°. Δ^{δ}-Heptylene, acetyl chloride, and aluminium chloride yield the *ketone*, $C_9H_{16}O$, b. p. 189—190°, D_4^{19} 0·8610, n_D 1·4521 (*semicarbazone*, m. p. 157°). *δ-Hydroxyheptane*, b. p. 154·5°, D_4^{20} 0·8183, n_D 1·4205. *δ-ε-Dibromoheptane*, b. p. 107°/15—17 mm., $D_4^{16\cdot5}$ 1·5250, n_D 1·5035. Δ^{α}-Octene, acetyl chloride, and aluminium chloride yield *Δγ-decylen-β-one*, $CH_3\cdot CO\cdot CH{:}CH\cdot[CH_2]_5\cdot CH_3$, b. p. 120—122°/38 mm., D_4^{21} 0·8681, n_D 1·4513, in 40% yield, the *semicarbazone* of which has m. p. 149°. Ethylene, acetyl chloride (or bromide), and aluminium chloride (or bromide) in hexane yield *Δ^{α}-buten-γ-one*, $CH_2{:}CH\cdot COMe$, b. p. 78—80°, D_4^{20} 0·8636, n_D 1·4086, which forms a *semicarbazone*, m. p. 140—141°. By-products of these reactions are halides, $C_nH_{2n+1}X$, and halogen-substituted ketones, $C_nH_{2n}X\cdot COMe$.

C. S.

Action of the Electric Discharge on Chloroform and Carbon Tetrachloride in Presence of Hydrogen, and also on Methyl Chloride. Adolphe Besson and L. Fournier (*Compt. rend.*, 1910, 150, 1118—1121. Compare this vol., ii, 406).—Losanitsch

(this vol., i, 1) has examined the action of the silent electric discharge on chloroform; the present communication describes a repetition of these experiments, in which a mixture of chloroform and hydrogen was employed and a more complete separation of the products effected. The following substances have been recognised in the dark oily mixture obtained: hexachloroethane (the predominating constituent), carbon tetrachloride, pentachloroethane, tetrachloroethylene, hexachloropropylene, heptachloropropylene, and octachlorobutylene. A similar mixture is obtained by the prolonged action of heat. A mixture of carbon tetrachloride with hydrogen gave practically the same products, and, in addition, a compound, $C_4H_2Cl_6$.

Methyl chloride submitted to the discharge in the absence of hydrogen gave a mixture containing dichloroethane, hexachloroethane, tetrachlorobutane, and indefinite fractions varying in composition from $C_3H_5Cl_3$ to $C_4H_5Cl_3$. W. O. W.

Apparatus for Absolute Alcohol. William H. Warren (*J. Amer. Chem. Soc.*, 1910, **32**, 698—702).—An apparatus is described for the preparation of absolute alcohol in the laboratory. It consists of an outer copper vessel, which serves as a constant-level water-bath, and an inner copper vessel for the alcohol. The latter is provided with a rubber stopper, through which passes a brass tube with two arms, each furnished with a stopcock. One of the arms is connected with a vertical condenser, and the other with a sloping condenser. Quick-lime and alcohol are placed in the inner vessel, and the stopcock is opened in the arm leading to the vertical condenser. The alcohol is boiled until dehydration is complete. The stopcock is then closed, whilst that in the arm leading to the sloping condenser is opened and the alcohol distilled off.

Experiments with this apparatus have shown that it is not possible to remove all the water from alcohol by means of lime, but alcohol of 99·94% strength can be obtained by boiling it for six hours before distilling. If the alcohol is left with the lime at the ordinary temperature for twenty-four hours, it is only necessary to boil it for five hours before distilling. The yield of alcohol can be increased by conducting the dehydration in two stages, and using each time a quantity of lime which is only slightly more than that theoretically required to combine with the water present. In this way, however, the alcohol cannot be obtained so strong as when the dehydration is carried out in one operation in presence of a large excess of lime.

E. G.

Theory of the Formation of Fusel Oil. [Production of Glycerol during Alcoholic Fermentation.] José R. Carracido (*Anal. Fis. Quim.*, 1909, **7**, 474—479).—In view of recent papers by Ehrlich (compare Abstr., 1907, ii, 383; 1908, i, 268; ii, 416), in which the formation of fusel oil by the action of yeast on leucine and *iso*leucine is demonstrated, the author refers to his paper (*Revista Acad. Sci. Madrid*, 1904, 1, 217) dealing with the mechanism of the production of glycerol during alcoholic fermentation. In this paper, which appears to have been overlooked, the formation of glycerol was attributed, not to the decomposition of sugar by the yeast, but to an

autolytic destruction of the yeast itself, probably owing to the action of an enzyme on the protein matter of the yeast cells. This view is strengthened by the fact that when egg-albumin is added to sugar which is undergoing fermentation by yeast, the proportion of glycerol produced is very greatly increased. W. A. D.

Complex Compounds of Glycols. Adolf Grün and E. Boedecker (*Ber.*, 1910, **43**, 1051—1062. Compare Grün and Bockisch, Abstr., 1908, i, 932).—The methyl derivatives of glycol give rise to complex metallic compounds in much the same manner as ethylene glycol itself. Some of the compounds are hygroscopic and difficult to isolate. All the compounds examined, including nitrates, chlorides, bromides, and sulphates of cobalt and nickel, contain three molecules of the glycol. They are much less stable than the corresponding metal ammonia salts; their aqueous solutions decompose rapidly, and even the alcoholic solutions are decomposed by alkalis, silver oxide, and sulphides.

Tri-ethylene-glycol-cobaltobromide, $[Co(C_2H_6O_2)_3]Br_2$, obtained by heating hydrated cobalt bromide and ethylene glycol for two hours on the water-bath, crystallises from alcohol in rose-red prisms, and melts at 79° to a deep blue liquid. Its solution in absolute alcohol is blue, and reacts with silver salts, yielding the corresponding chloride and nitrate. When kept over concentrated sulphuric acid, the compound loses ethyleneglycol, and yields *diethylene-glycol-cobaltobromide*

$$CoBr_2,2C_2H_4(OH)_2,$$

as lilac-coloured crystals, m. p. 74°. The *chloride*, $[Co(C_2H_6O_2)_3]Cl_2$, forms blue pyramids, m. p. 68°. It yields a *monohydrate* in the form of rose-coloured crystals, m. p. 63°, and when kept over phosphoric oxide under reduced pressure slowly loses ethylene glycol, yielding *diethylene-glycol-cobaltochloride*, $CoCl_2,2C_2H_6O_2$, as dark lilac-coloured crystals. The *nitrate*, $[Co(C_2H_6O_2)_3](NO_3)_2$, forms deep red crystals, m. p. 52°.

Triethylene-glycol-nickelonitrate, $[Ni(C_2H_6O_2)_3](NO_3)_2$, forms grass-green crystals, m. p. 78°; the *sulphate*, $[Ni(C_2H_6O_2)_3]SO_4,H_2O$, is pale green in colour, and when heated at 100° gives up either 1 molecule of glycol or a molecule of glycol plus water, yielding *diethylene-glycol-nickel sulphate hydrate*, $NiSO_4,2C_2H_6O_2,H_2O$, or the corresponding anhydrous compound, both of which have an apple-green colour.

The complex compounds obtained from glycerol-α-monochlorohydrin do not crystallise; they have been obtained as oils or jellies, except *triglycerol-α-chlorohydrin-nickelochloride*, $[Ni(C_3H_7ClO_2)_3]Cl_2$, which was obtained as green crystals after the lapse of a year.

Tri-glycerol-α-chlorohydrin-chromichloride, $[Cr(C_3H_7ClO_2)_3]Cl_3,3H_2O$, obtained from the two isomeric chromic chloride hexahydrates, forms a syrupy liquid, which appears moss-green in transmitted light, but nearly black in reflected light. The blue chromic chloride yields first a bluish-violet complex salt, but this passes rapidly into the green compound.

Tripropylene-glycol-cobaltochloride, $[Co(C_3H_8O_2)_3]Cl_2$, has a deep blue colour, but turns red on exposure to the air. The corresponding *nitrate* forms a ruby-red, flocculent mass.

Tripropylene-glycol-nickelo-sulphate, $[Ni(C_3H_8O_2)_3]SO_4$, forms a grass-green, vitreous mass.

β-Methylbutylene $\beta\gamma$-glycol yields crystalline, complex salts, but these have not been analysed.

Tripinacone-cobaltonitrate, $[Co(C_6H_{14}O_2)_3](NO_3)_2,2H_2O$, forms well-developed, reddish-violet, monoclinic prisms, m. p. 130°. The *monohydrate* is rose-coloured. The *bromide*, $[Co(C_6H_{14}O_2)_3]Br_2,2H_2O$, forms dark red, crystalline plates, m. p. 136°.

Tripinacone-cobalto-tetrachlorocobaltoate, $[Co(C_6H_{14}O_2)_3]CoCl_4$, obtained by the action of a concentrated solution of cobalt chloride on pinacone hydrate and methyl alcohol, has a deep blue colour when freshly prepared, but becomes sky-blue when exposed to the air or kept over sulphuric acid, owing to the loss of methyl alcohol.

Catechol does not appear to form complex metallic salts (compare Ley and Erler, Abstr., 1908, i, 177). J. J. S.

Glycerolates of the Alkaline-earth Metals. Adolf Grün and J. Husmann (*Ber.*, 1910, **43**, 1291—1298).—The hydroxides of calcium, strontium, and barium combine with glycerol, yielding compounds of the type $\left[Ca:::\left(\begin{matrix}OH\cdot CH_2\\ OH\cdot CH\cdot CH_2\cdot OH\end{matrix}\right)_3\right]OH_2$, in which the glycerol forms a complex radicle with the metallic atom, owing to the subsidiary valencies of two hydroxyl groups of the glycerol. The calcium derivative has been described previously (Grün and Bockisch, Abstr., 1908, i, 935). *Triglycerol barium hydroxide* has been obtained in a crystalline form by dissolving the anhydrous compound in methyl alcohol and adding acetone. It is extremely hygroscopic, and readily absorbs carbon dioxide. The *strontium hydroxide triglycerolate* is similar. *Diglycerol calcium hydroxide hydrate*,

$$Ca(OH)_2,2C_3H_8O_3,H_2O,$$

is formed when calcium hydroxide and water are shaken in the cold with glycerol. It is a yellowish-white, crystalline mass, readily soluble in water, and when heated at 130° loses a molecule of glycerol.

Triglycerol calcium chloride, $[Ca,3C_3H_8O_3]Cl_2$, obtained by dissolving anhydrous calcium chloride in hot glycerol, sets to a vitreous mass, and can be purified by solution in alcohol and precipitation with acetone. The crystalline compound is formed by dissolving hydrated calcium chloride in glycerol and keeping over sulphuric acid. It forms brilliant, transparent cubes, m. p 76°, and is extremely hygroscopic.

Tetraglycerol calcium nitrate, $Ca(NO_3)_2,4C_3H_8O_3$, also forms colourless, transparent crystals, m. p. 72°, but when strongly heated decomposes with explosive violence. The chlorides and nitrates of strontium and barium are not so soluble in glycerol as the calcium salts, and it has not been found possible to prepare crystalline glycerol derivatives. The following products were obtained by adding acetone to the alcoholic solutions: $SrCl_2,7C_3H_8O_3$; $Sr(NO_3)_2,8C_3H_8O_3$, and

$$BaCl_2,7C_3H_8O_3,2H_2O.$$

J. J. S.

Ethyl Ether of Allylcarbinol. H. Pariselle (*Compt. rend.*, 1910, **150**, 1056—1058. Compare Abstr., 1909, i, 282, 691; Lespieau, Abstr., 1907, i, 580).—The *ether*, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$ has been obtained by acting on magnesium allyl bromide with chloromethyl ethyl ether; the compound has b. p. 90°, D^0 0·811, n_D^{17} 1·396, and forms a *dibromo*-derivative, $C_6H_{12}OBr_2$, b. p. 98°/13 mm., D^0 1·76, n_D^{15} 1·512. When the latter is boiled with water, 3-hydroxytetrahydrofuran is formed, together with *αβ-dihydroxy-δ-ethoxybutane*,

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OEt,$$

b. p. 130°/14 mm.; the *diphenylurethane* has m. p. 98—99°.

Hypochlorous acid converts the ether of allylcarbinol into a liquid, b. p. 88—90°/12 mm., consisting of *α-chloro-β-hydroxy-δ-ethoxybutane*, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OEt$, D^0 1·1138, n_D^{17} 1·45, with traces of the ether, $OH{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$. Hydrogen bromide converts the product into *α-chloro-δ-bromo-β-hydroxybutane*, b. p. 103—106°/13 mm., n_D^{15} 1·52, D^0 1·71. The corresponding epibromohydrin on treatment with potassium hydroxide yields the *ether*, $\begin{matrix}CH_2\\ |\\ O\text{---}\end{matrix}\!\!>\!CH{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$, b. p. 146—147°. W. O. W.

Synthesis of the Diprimary Glycols, $HO(CH_2)_{n+2}{\cdot}OH$, by means of the Dihaloid Compounds, $X(CH_2)_n{\cdot}X$. R. Dionneau (*Bull. Soc. chim.*, 1910, [iv], 7, 327—329).—Hamonet's reaction (Abstr., 1904, i, 401) applied to the dihaloid derivatives of the paraffins furnishes the corresponding alkyl ethers of the glycols, provided that the dihaloid compounds yield true magnesium derivatives of the type $MgBr{\cdot}[CH_2]_n{\cdot}MgBr$. The dimethyl ethers of heptamethylene and octamethylene glycols have been prepared in this manner.

α-ε-Dibromopentane dissolves a little less than the quantity of magnesium requisite to form the compound $BrMg{\cdot}[CH_2]_5{\cdot}MgBr$, and the liquid reacts with chloromethoxymethane to form *αη*-dimethoxyheptane, b. p. 104—105°/35 mm. or 201°/760 mm. (compare Abstr., 1907, i, 747).

αζ-Dibromohexane by similar reactions furnishes *aθ*-dimethoxyoctane, b. p. 121°/35 mm. or 221°/760 mm., and *aθ-diamyloxyoctane*, b. p. 212°/35 mm. Both these ethers furnish with hydrobromic acid the corresponding *aθ*-dibromo-octane of Solonina (Abstr., 1899, i, 561). T. A. H.

Synthesis of Ethers of Hexane-*aζ*-diol: Production of Hexylenic Ethers, $C_6H_{11}{\cdot}OR$. R. Dionneau (*Bull. Soc. chim.*, 1910, [iv], 7, 329—330).—The action of sodium on iodo-ethers (Hamonet, Abstr., 1903, i, 251, 306; Dionneau, Abstr., 1906, i, 134; 1907, i, 747) is more complex than von Braun and Trümpler (this vol., i, 25) suppose, some allyl ether being always formed as well as alkyloxy-derivatives of hexylene in addition to the glycol ethers when alkyloxy-derivatives of iodopropane are used.

Phenoxyhexylene, b. p. 147°/35 mm. or 249°/760 mm., obtained as a by-product in the action of sodium on phenoxyiodopropane, could

not be obtained pure (compare Solonina, Abstr., 1899, i, 561). It combines with one mol. of hydrogen iodide in the cold, forming the *compound*, $OPh{\cdot}C_6H_{12}I$, b. p. 198°/25 mm., and when warmed with excess of hydriodic acid yields a *di-iodohexane*, b. p. 160°/33 mm., which remains liquid at 0°, and is not identical with αζ-di-iodohexane. *Methoxyhexylene*, $OMe{\cdot}C_6H_{11}$, b. p. 123°/760 mm., similarly obtained, gives a *dibromide*, b. p. 148°/30 mm., and *ethoxyhexylene*, b. p. 140°/760 mm., yields a *dibromide*, m. p. 154°/30 mm. T. A. H.

Isomeric Platinum Compounds of Organic Sulphides. Leo Tschugaeff and W. Subbotin (*Ber.*, 1910, **43**, 1200—1205).—Compounds of platinous chloride with organic sulphides $PtCl_2,2R_2S$, exist in two modifications; in the case of $PtCl_2,2Me_2S$, a third insoluble, red-coloured isomeride, the γ-salt, has been described. Various formulæ have been ascribed to this isomeride; both Blomstrand (Abstr., 1889, 230) and Klason (Abstr., 1895, i, 488) considered the possibility of it being an analogue of the green Magnus salt, and having the formula $[Pt4Me_2S]PtCl_4$, but abandoned this constitution.

It is now shown that on shaking the red γ-salt in aqueous solution with Reiset's chloride, $(Pt4NH_3)Cl_2$, it becomes green, and is converted into the Magnus salt, $[Pt4NH_3]PtCl_4$. Accordingly, the above constitution is established for the red γ-salt. The two other isomerides derived from methyl sulphide do not interact with Reiset's chloride.

Similar compounds are formed by platinum chloride and 1 : 2-dithioglycol ethers. Thus, ethylene dithioglycol ether when shaken with potassium platinichloride in cold aqueous solution forms small, flesh-coloured prisms or needles of the compound $PtCl_2,C_2H_4(SEt)_2$. When shaken with the Reiset's salt, the red isomeride is converted into the green Magnus salt. When the red compound is warmed with water, it is slowly converted into a yellow isomeride; the same change takes place more quickly in the dry state at 136·5°. The yellow isomeride has m. p. 188°, and does not react with Reiset's salt. It is formed directly when potassium platinichloride and disulphide interact at 100°.

Similarly, *n*-propyl 1 : 2-dithioglycol ether reacts with potassium platinichloride, forming a red substance, which is transformed into a yellow isomeride at higher temperatures, and yields Magnus salt with Reiset's chloride. In this case the Magnus salt is first obtained in a red modification, which slowly, or more quickly on heating, changes into the normal green form. E. F. A.

Glucinum Formates. Sebastian M. Tanatar (*Ber.*, 1910, **43**, 1230—1231).—Normal glucinum formate, $Gl(CHO_2)_2$, may be obtained by the solution of glucinum carbonate in 50 or 90% formic acid and evaporation of the solution at 100—110°, or in a desiccator. This is in contradistinction to the indirect methods which have to be used to prepare the normal acetate and propionate (compare Abstr., 1907, i, 888).

Glucinum formate is insoluble in organic solvents. The aqueous solution undergoes hydrolysis only after prolonged boiling, the resulting

basic salt having a composition intermediate between $Gl(CHO_2)_2$ and $Gl_4O(CHO_2)_6$. On heating under diminished pressure (30—35 mm.), the normal salt gives a sublimate of the basic salt, $Gl_4O(CHO_2)_6$.

T. S. P.

Ethyl Acetate. Alex. Bogojawlenski and J. Narbutt (*J. pr. Chem.*, 1910, [ii], **81**, 420—421).—The preparation of ethyl acetate by the aid of anhydrous copper sulphate (Habermann and Brezina, Abstr., 1909, i, 873) has been described by the authors (Abstr., 1905, i, 854).

C. S.

Solidification of Binary Mixtures of the Saturated Monobasic Fatty Acids and Water. Rezsö Balló (*Zeitsch. physikal. Chem.*, 1910, **72**, 439—450).—The fact that formic and acetic acids produce abnormally small depressions of the freezing point of water has been ascribed by previous observers to association of the acids, but the author now shows that it is due to the formation of solid solutions of water and the respective acids.

The mixtures of acid and water were partly frozen, the mother liquor removed by filtration and centrifugal action, portions of the solid mass melted, and the liquid removed in order to secure as complete a separation of the mother liquor as possible; the crystals were then analysed. In spite of these precautions, evidence was obtained that the separation from the mother liquor was by no means complete, so that the results are only qualitative.

Acetic acid and water form four series of mixed crystals, which separate from solutions containing 0—40%, 40—59%, 59—77%, and 77—100% by weight of the acid respectively. The results with the other acids are similar, except that propionic acid appears to form a definite compound with water of the formula $H_2O,11C_2H_5\cdot CO_2H$. The eutectic temperature of mixtures of butyric acid and water is $-10{\cdot}4°$; the eutectic mixture contains 88·91% by weight of the acid. G. S.

Essence of Cocoanut Butter. Composition of Cocoanut Oil. Albin Haller and A. Lassieur (*Compt. rend.*, 1910, **150**, 1013—1019).—Commercial cocoanut oil owes its unpleasant odour to the presence of hexoic, octoic, and decoic acids arising from hydrolysis of the glycerides, and also to certain neutral compounds, chiefly methyl heptyl ketone and methyl nonyl ketone. The presence of a small quantity of an optically active aldehyde has also been recognised. The odorous substances may be separated by distillation in superheated steam, and constitute the mixture known as essence ("échappées") of cocoanut butter. The ketones appear to exist in the butter, and not to be formed during distillation.

When methyl nonyl ketone is hydrogenated in presence of reduced nickel at 250—300°, it yields a *hydrocarbon*, C_9H_{20}, b. p. 150—155°/760 mm., and a *pinacolin*, m. p. 27°, to which the constitution

$$C_9H_{19}\cdot CMe_2\cdot CO\cdot C_9H_{19}$$

is ascribed; this substance is unaltered by alkaline hypobromite, but forms an *oxime*, b. p. 233—237°, and a *semicarbazone*, m. p. 225—227°.

W. O. W.

Syntheses of Symmetrical Monoglycerides. Adolf Grün (*Ber.*, 1910, **43**, 1288—1291).—α-Monoglycerides,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot COR,$$

have been synthesised already by Krafft (Abstr., 1904, i, 137) and Guth (Abstr., 1903, i, 225). The author has prepared a number of β-monoglycerides, $COR\cdot O\cdot CH(CH_2\cdot OH)_2$, by the action of β-monochlorohydrin on the salts of fatty acids. The same glycerides have also been prepared more conveniently from the αγ-dichlorohydrin: first converting it into the compound $COR\cdot O\cdot CH(CH_2Cl)_2$ by the action of an acyl chloride, and then replacing the two chlorine atoms by hydroxyl through the agency of silver nitrite (compare Grün and Theimer, Abstr., 1907, i, 464).

β-Lauryl-αγ-dichlorohydrin, $C_{11}H_{23}\cdot CO\cdot O\cdot CH(CH_2Cl)_2$, forms a yellow, mobile oil, and when heated with its own weight of silver nitrate in a stream of hydrogen at 120°, yields *β-monolaurin*,

$$C_{11}H_{23}\cdot CO\cdot O\cdot CH(CH_2\cdot OH)_2,$$

which crystallises in glistening needles, m. p. 61°, after sintering at 58°. When kept for some time, it has m. p. 57·5°. *β-Monopalmitin*, $C_{15}H_{31}\cdot CO\cdot O\cdot CH(CH_2\cdot OH)_2$, crystallises in plates, m. p. 74°, but after several months the m. p. is 69·5°. J. J. S.

Partial Hydrogenation of Acids in the Stearolic Series and Isomerism of their Hydriodo-derivatives. Albert Arnaud and Swigel Posternak (*Compt. rend.*, 1910, **150**, 1130—1132).—Holt (Abstr., 1892, 962) has stated that behenolic acid is reduced by zinc dust and acetic acid to brassidic acid; this author's experiments have now been repeated, but without success. Reduction, however, was accomplished by passing hydrogen iodide into the fused acid and heating the resulting iodo-derivative with zinc dust and acetic acid for twelve to twenty-four hours. Other stearolic acids have been reduced in the same way: thus tariric acid yields *Δ⁶-elaidic acid*, $C_{18}H_{34}O_2$, for which the name *tarelaidic acid* is suggested; it crystallises in prisms, m. p. 52·5°, and on oxidation furnishes *cis-ζη-dihydroxystearic acid*, $C_{18}H_{36}O_4$, m. p. 117·5°.

The addition of hydrogen iodide to stearolic acids appears to take place in such a way that two isomeric derivatives of the types CHR:CHR′ and CHR′:CHR are formed. The separation of the two isomerides produced in this way from stearolic and behenolic acids is described. The iodoelaidic acids have m. p. 39° and 23—24°, whilst the corresponding derivatives of brassidic acid have m. p. 48° and 37—38° respectively. W. O. W.

Condensation of Secondary Amines with Ethyl γ-Bromo-αα-dimethylacetoacetate. Henri Gault and G. Thirode (*Compt. rend.*, 1910, **150**, 1123—1125).—*Ethyl γ-diethylamino-αα-dimethylacetoacetate*, $NEt_2\cdot CH_2\cdot CO\cdot CMe_2\cdot CO_2Et$, b. p. 118°/14 mm., has been prepared by adding diethylamine (2 mols.) to ethyl γ-bromo-αα-dimethylacetoacetate in dry ether (Conrad, Abstr., 1897, i, 321; 1899, i, 193). The substance has not yielded crystalline derivatives, and undergoes decomposition when heated with phenylhydrazine; on hydrolysis with dilute acids, it furnishes *diethylaminomethyl* isopropyl

ketone, $NEt_2 \cdot CH_2 \cdot COPr^{\beta}$, b. p. 75°/14 mm., 182° under atmospheric pressure.

Ethyl γ-ethylanilino-αα-dimethylacetoacetate,

$$NEtPh \cdot CH_2 \cdot CO \cdot CMe_2 \cdot CO_2Et,$$

b. p. 189°/13 mm., furnishes a 3-*ethylanilinomethyl*-1-*phenyl*-4 : 4-*dimethylpyrazolone*, m. p. 77°, and gives on hydrolysis *ethyl anilinomethyl* iso*propyl ketone*, $NEtPh \cdot CH_2 \cdot COPr^{\beta}$, a colourless liquid, b. p. 154°/14 mm., becoming yellow on exposure to light; the unstable *phenylhydrazone* has m. p. 87°. W. O. W.

Velocity of Electrolytic Oxidation of Certain Organic Acids. F. Ageno and G. Donini (*Gazzetta*, 1910, 40, i, 21—31).—The authors discuss previous investigations on the velocity of reaction in electrochemical processes, more especially reduction processes. In their own experiments on the electrolytic oxidation of organic acids, an apparatus was employed similar to that used by Åkerberg (Abstr., 1902, ii, 488), the cathode of smooth platinum being surrounded by a small glass bell in order to allow the hydrogen liberated to escape without coming into contact with the anode, which was composed of a peroxide. In the case of oxalic acid, with an anode of lead peroxide, the unimolecular reaction constant gradually increases, whilst the values of Goldschmidt's constant, $K_1 = 3(\sqrt[3]{a} - \sqrt[3]{a-x})/t_1$ (*Zeitsch. Elektrochem.*, 1900, **7**, 263), remain moderately constant. The velocity of reaction is hence proportional to C^3, which expresses the concentration in a section, so that the reaction takes place at the surface of the electrode. From the beginning the action consists of an oxidation due to the oxygen evolved, the anode acting as a catalyst; this behaviour is in complete agreement with the observation that the oxidation of oxalic acid by lead peroxide proceeds spontaneously at the ordinary temperature, and with the course of the anode-potential, which, apart from an initial depolarising action on the electrode, remains constant. With sodium hydrogen oxalate, the velocity-constants are considerably less than with oxalic acid, so that it appears probable that the non-dissociated acid and the ion HC_2O_4 are preferably oxidised, this confirming the hypothesis that the oxidation is a secondary phenomenon of a chemical nature occurring under the specific catalytic influence of the electrode.

With an anode of manganese dioxide, the velocity of oxidation and the course followed by the anode-potential are perfectly analogous to those obtained with lead peroxide. When an anode of nickel or cobalt peroxide is employed in a solution rendered alkaline by sodium hydroxide, no oxidation of oxalic acid takes place, the C_2O_4 ion remaining unattacked by the oxygen developed electrolytically.

Malonic and succinic acids are not altered by the anodic oxygen liberated at an anode of platinised platinum or of lead or manganese dioxide, but the alkali salts of these acids undergo oxidation (compare Petersen, Abstr., 1898, i, 352). For the oxidation of the potassium salts at an electrode of lead peroxide, neither the formula for a unimolecular reaction nor Goldschmidt's formula gives a constant value for the reaction constant, several reactions apparently occurring simultaneously at the electrode. T. H. P.

Hydrazine Oxalates. J. W. Turrentine (*J. Amer. Chem. Soc.*, 1910, **32**, 577—588).—Two *oxalates* of hydrazine, $2N_2H_4,H_2C_2O_4$ and $N_2H_4,H_2C_2O_4$, are described. The former crystallises in needles and plates, and is soluble to the extent of 2·009 grams in 1 gram of water at 35°. When heated in a capillary tube, it begins to decompose at 130°, and afterwards melts to a clear liquid, which solidifies on cooling with production of a substance of m. p. about 150°. The decomposition of the salt by heat has been studied under various conditions, and it has been found that the decomposition products are water, ammonia, hydrogen cyanide, hydrazine, carbon dioxide and monoxide, nitrogen, and carbon. A complex hydrazine *compound* is also formed as a white, crystalline sublimate.

The other salt, $N_2H_4,H_2C_2O_4$, forms lustrous, monoclinic needles [$\beta = 63°20'$], and is soluble only to the extent of 0·0204 gram in 1 gram of water at 22·5°, but is readily soluble in boiling water. When heated in a capillary tube at 200°, it is converted into a liquid which does not solidify on cooling. On destructive distillation, it yields water, ammonia, hydrogen cyanide, carbon dioxide and monoxide, nitrogen, and carbon, together with a white sublimate which appears to be an ammonium compound. If the decomposition is effected in a sealed tube, a substance is obtained which is probably a hydrazine salt of an acid containing carbon. When this oxalate is dissolved in water, one-half of the acid is liberated and can be titrated with alkali. E. G.

Compounds with a Branched Chain. III. Mlle. Germaine Freylon (*Ann. Chim. Phys.*, 1910, [viii], **20**, 58—115. Compare this vol., i, 296).—The author describes the preparation of compounds with highly branched chains, and points out the influence of such chains in modifying the general properties of these substances.

The following derivatives of *iso*butylmalonic acid are mentioned: the *dimethyl* ester, b. p. 101°/15 mm.; *diethyl* ester, b. p. 119—120°/16 mm.; the *dichloride*, b. p. 83—85°/22 mm.; the *diamide*, needles, m. p. 195—196°.

Di*iso*butylmalonic acid has m. p. 157—158°; Perkin and Bentley (Trans., 1898, **73**, 61) give 145—150°, but their preparation probably contained some *monomethyl* ester, b. p. 155—160°/12 mm. The *methyl ethyl* ester has b. p. 140—142°/18 mm.; the diethyl ester, b. p. 148—150°/14 mm.; the *dichloride*, b. p. 136—140°/20 mm.; the *diamide* forms pearly leaflets, m. p. 280—281°. γ-Methyl-α-*iso*butylvaleric acid, obtained by heating the foregoing acid, has b. p. 139—141°/18 mm., D_0^4 0·913 (compare Perkin and Bentley, *loc. cit.*); the *methyl* ester has b. p. 87—89°/15 mm.; the *ethyl* ester, b. p. 91—93°/13 mm., D_0^4 0·870; the *ketonic* ester,

$$(C_4H_9)_2CH\cdot CO_2\cdot CH_2\cdot COMe,$$

b. p. 135—140°/13 mm., forms a *semicarbazone*, m. p. 119—120° (compare Locquin, Abstr., 1904, i. 644). The corresponding *ketonic* ester of γ-methylvaleric acid, $CH_2Pr^{\beta}\cdot CH_2\cdot CO_2\cdot CH_2\cdot COMe$, forms a *semicarbazone*, m. p. 70—71°.

γ-Methyl-α-*iso*butylvaleric acid has also been characterised by means of the *chloride*, b. p. 80—83°/13 mm., and the *amide*, which crystallises in lamellæ, m. p. 74—75°; the substance described by Perkin and Bentley under this name is shown to be γ-methylvaleramide. When the acid chloride is treated successively with bromine and alcohol, *ethyl α-bromo-γ-methyl-α-iso*butylvalerate,

$$CBr(CH_2Pr^{\beta})_2\cdot CO_2Et,$$

b. p. 130—135°/14 mm., is obtained; the corresponding *bromoamide* has m. p. 77—78°, and yields di*iso*butyl ketone when treated according to the method of Mannich and Zernich (Abstr., 1908, i, 399).

Ethyl γ-methyl-α-*iso*butylvalerate, on reduction with sodium and alcohol, forms δ-methyl-β-*iso*butylpentanol, the *pyruvate* of which has b. p. 135—140°/21 mm., and gives a *semicarbazone*, m. p. 159—160°; the *phenylurethane* has m. p. 54—55°.

The reduction of ethyl di*iso*butylmalonate leads to the formation of the foregoing pentanol, together with di*iso*butyltrimethylene glycol and *γ-methyl-α-hydroxymethyl-α-*iso*butylvaleric acid*,

$$OH\cdot CH_2\cdot C(CH_2\cdot CHMe_2)_2\cdot CO_2H,$$

m. p. 83—84°. The *methyl* ester of this compound has b. p. 121—123°/11 mm., D_0^4 0·973; the *ethyl* ester, b. p. 133—135°/15 mm., was prepared by the action of formaldehyde on α-bromo-γ-methyl-α-*iso*butylvalerate in presence of magnesium amalgam; at the same time there is formed *ethyl ββδδ-tetra*iso*butylacetoacetate*,

$$CH(CH_2Pr^{\beta})_2\cdot CO\cdot C(CH_2Pr^{\beta})_2\cdot CO_2Et,$$

m. p. 59—60°, a very stable substance which has not yet been hydrolysed.

The application of Grignard's reaction to ethyl γ-methyl-α-*iso*butylvalerate results in the formation of *βε-dimethyl-γ-*iso*butylhexan-β-ol*, $CH(CH_2Pr^{\beta})_2\cdot CMe_2\cdot OH$, b. p. 93—94°/7 mm.; pyruvic acid converts this into *βε-dimethyl-γ-*iso*butyl-Δ$^{\beta}$-hexene*, b. p. 65°/10 mm.; the corresponding *diphenylurethane* has b. p. 240°. Magnesium methyl iodide acts on ethyl di*iso*butylmalonate, forming *γ-methyl-α-hydroxy-*iso*propyl-α-*iso*butylvaleric acid*, $OH\cdot CMe_2\cdot C(C_4H_9)_2\cdot CO_2H$, b. p. 155—160°/15 mm., and *ε-methyl-γ-*iso*butylhexan-β-one*,

$$(CH_2Pr^{\beta})_2CH\cdot COMe,$$

b. p. 82—84°/12 mm. The synthesis of this ketone has been effected by three other methods, and its constitution determined from a study of its oxidation products; the *semicarbazone* has m. p. 138—139°, the *oxime*, b. p. 123—126°/10 mm.

By dehydrogenating δ-methyl-β-*iso*butylpentanol in presence of reduced copper, α-*iso*butyl*iso*hexoaldehyde, $CH(CH_2Pr^{\beta})_2\cdot CHO$ (Behal and Sommelet, Abstr., 1904, 222), has been obtained, accompanied by a bimolecular polymeride. The aldehyde has b. p. 82—83°/18 mm., D_0^4 0·825, and forms an *oxime*, b. p. 125—126°/20 mm., and a *semicarbazone*, m. p. 139—140°, identical with that obtained from the polymeride, $C_{20}H_{40}O_2$, b. p. 160—170°/20 mm. W. O. W.

Dibromomaleic Anhydride. I. Otto Diels and Martin Reinbeck (*Ber.*, 1910, **43**, 1271—1279).—Attempts have been made to

eliminate bromine from dibromomaleic anhydride and iodine from di-iodomaleic anhydride, but without success.

Ethyl malonate readily combines with the dibromo-anhydride, yielding a diethyl ester of *αβ-dibromo-Δ$^{\alpha}$-butylene-γ-one-αδδ-tricarboxylic acid*, $CO_2H{\cdot}CBr{:}CBr{\cdot}CO{\cdot}CH(CO_2Et)_2$, which is readily hydrolysed to dibromomaleic acid and ethyl malonate, but when heated at 100° with glacial acetic acid saturated at 0° with hydrogen bromide, it yields 4 : 5-dibromo*cyclo*pentene-1 : 3-dione, $CH_2<\begin{matrix}CO{\cdot}CBr\\ \|\\ CO{\cdot}CBr\end{matrix}$, the parent substance of Wolff and Rüdel's tribromo*cyclo*pentenedione (Abstr., 1897, i, 215).

A good yield of dibromomaleic acid can be obtained by oxidising mucobromic acid at low temperatures (25—30°) with an amount of nitric acid (D 1·5) necessary for solution (compare Hendrixson. Abstr., 1890, 958). The acid has m. p. 142°, the m. p.'s previously given, namely, 120° to 125°, are low, owing to the presence of small amounts of anhydride.

Di-iodomaleic anhydride, $C_4O_3I_2$, obtained by the action of sodium iodide on an acetone solution of the dibromo-anhydride, crystallises in glistening, yellow needles, m. p. 116°.

Methyl hydrogen dibromomaleate, $CO_2H{\cdot}CBr{:}CBr{\cdot}CO_2Me$, prepared by the action of methyl alcohol on the anhydride, crystallises in long slender needles, m. p. 78—79°.

Diethyl hydrogen αβ-dibromo-Δ$^{\alpha}$-butylene-γ-one-αδδ-tricarboxylate, $CO_2H{\cdot}CBr{:}CBr{\cdot}CO{\cdot}CH(CO_2Et)_2$, crystallises in small, rhombic plates, m. p. 76—77°, and yields a *potassium* salt, which also crystallises in plates.

4 : 5-*Dibromo*cyclo*pentene*-1 : 3-*dione*, $C_5H_2O_2Br_2$, crystallises in pale yellow, nacreous plates, m. p. 157—158°, and reacts with a chloroform solution of bromine at the ordinary temperature, yielding 2 : 2 : 4 : 5-*tetrabromo*cyclo*pentene*-1 : 3-*dione*, $CBr_2<\begin{matrix}CO{\cdot}CBr\\ \|\\ CO{\cdot}CBr\end{matrix}$, which crystallises in yellow needles, m. p. 140—143°.

Dimethyldibromomaleide, $O<\begin{matrix}CMe_2{\cdot}CBr\\ \|\\ CO{-}{-}CBr\end{matrix}$, obtained by the action of magnesium methyl iodide on an ethereal solution of dibromomalcic anhydride and subsequent treatment with dilute sulphuric acid, crystallises in compact prisms, m. p. 129—130°. J. J. S.

Inertia of Crystallisation of Tartrate Mother Liquors. P. Carles (*Bull. Soc. chim.*, 1910, [iv], 7, 326—327).—Calcium tartrate of commerce, containing iron, is often difficult to use as a source of tartaric acid, since on addition of sulphuric acid complex iron compounds are formed, which inhibit crystallisation of the tartaric acid. These may be eliminated by adding enough potassium ferrocyanide to precipitate all the iron. The filtrate from the precipitated Prussian-blue then usually deposits crystals of tartaric acid on evaporation. A little hydrocyanic acid is evolved in the reaction, so that the operation should be conducted in the open air.

T. A. H.

Interchange of Alkyl Groups in Acid Esters. Telemachios Komnenos (*Monatsh.*, 1910, **31**, 111—122).—By the interaction of sodium ethoxide, ethyl malonate and iodine, ethyl ethanetetracarboxylate, m. p. 77°, is formed. When sodium methoxide was substituted for the ethoxide, colourless, glistening crystals, m. p. 135°, were obtained, together with a viscid oil. The crystals proved to be tetramethyl ethanetetracarboxylate (compare Walker, Trans., 1895, **67**, 770), which may also be obtained by the action of sodium methoxide on ethyl ethanetetracarboxylate, and, alternatively, the methyl ester is converted by sodium ethoxide into the ethyl ester. E. F. A.

Ester Acids of Thiocarboxylic Acids with Aliphatic Alcohol Acids. IV. Preparation of Rhodanins. Bror Holmberg (*J. pr. Chem.*, 1910, [ii], **81**, 451—465. Compare Abstr., 1909, i, 286).—Two methods for the preparation of rhodanins are described. In one a dithiocarbamate is treated with an aqueous solution of an alkali salt of a halogen-substituted acid, and the solution of the resulting substituted dithiocarbamate is acidified by acetic acid, whereby the rhodanin is slowly precipitated (*loc. cit.*). The second method, which is more elegant but less widely applicable, depends on the fact that hot aqueous solutions of the trithiocarbodiglycollates of certain primary amines decompose into thioglycollic acid and thiocarbamylthioglycollic acids, the latter of which yield rhodanins: $CS(S\cdot CH_2\cdot CO_2H)_2 + R\cdot NH_2 \longrightarrow SH\cdot CH_2\cdot CO_2H +$

$$NHR\cdot CS\cdot S\cdot CH_2\cdot CO_2H \longrightarrow S\!<\!\begin{matrix}CH_2\cdot CO\\ |\\ CS\!-\!-\!NR\end{matrix}.$$

In addition to β-methylrhodanin, *N*-ethylrhodanin, *N*-phenylrhodanin, *N*-benzylrhodanin, *N*-*o*-tolylrhodanin, the corresponding *m*- and *p*-isomerides, *N*-phenyl-β-methylrhodanin, *N*-aminorhodanin, and *N*-anilinorhodanin, the following new compounds have been prepared (by the second method): N-*o*-*Methoxyphenylrhodanin*, $OMe\cdot C_6H_4\cdot N\!<\!\begin{matrix}CS\!-\!S\\ |\\ CO\cdot CH_2\end{matrix}$, m. p. 142·5—143°, and the para-*isomeride*, m. p. 155·5—156°, from *o*- and *p*-anisidine respectively, and N-p-*bromophenylrhodanin*, m. p. 164—165°, from *p*-bromoaniline; α- and β-naphthylamines yield only the corresponding dinaphthylthiocarbamides. C. S.

Glutardialdehyde. Carl D. Harries (*Ber.*, 1910, **43**, 1194. Compare Abstr., 1908, i, 517).—The dioxime of this substance forms long, white needles, m. p. 171°. The m. p. of the nitrophenylhydrazone formerly described can be raised by recrystallisation from toluene to 160—161°. R. V. S.

Tautomerism of Aliphatic Ketones. V. H. Hâncu (*Ber.*, 1910, **43**, 1193).—Polemical. A reply to Ostrogovich (Abstr., 1909, i, 764). The figures criticised by the latter were not the actual experimental results; these are now quoted, and are in agreement with the theoretical values. R. V. S.

Thalloacetylacetone. Eduard Kurowski (*Ber.*, 1910, **43**, 1078—1079).—Thalloacetylacetone, prepared by boiling thallium

carbonate with acetylacetone in alcoholic solution, crystallises in colourless, flat needles, which are transparent in ordinary light, and show a marked interference coloration in polarised light; m. p. 160° (decomp.). Very characteristic is the formation of a voluminous, orange precipitate with a few drops of carbon disulphide in alcohol or benzene solution; this affords a very delicate test for carbon disulphide, and similar, although differently coloured, precipitates are obtained with other organic sulphur compounds. E. F. A.

Condensation of Pinacolin with Esters. François Couturier (*Compt. rend.*, 1910, 150, 928—930. Compare Abstr., 1905, i, 570).—Further proof of the ketonic character of pinacolin is afforded by the fact that this substance undergoes condensation with esters in presence of sodium or sodium ethoxide, giving compounds having all the characteristics of β-diketones, and yielding *iso*oxazoles with hydroxylamine.

ββ-Dimethylhexan-γε-dione, $CMe_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, prepared from pinacolin and ethyl acetate, has b. p. 168°, D^0 0·933, and develops an intense red coloration with ferric chloride. The *sodium* and *copper* salts are crystalline, the latter having m. p. 175°; 5-*methyl*-3-tert.-*butyl*isoo*xazole*, $C_8H_{13}ON$, has m. p. 107°, the *phenylhydrazone*, m. p. 85°.

Ethyl trimethylacetylpyruvate, $CMe_3{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Et$, obtained from ethyl oxalate, has b. p. 124°/13 mm., and forms a *copper* salt crystallising in deep green prisms, m. p. 162°; *ethyl* 3-tert.-*butyl*iso-*oxazole*-5-*carboxylate* forms needles, m. p. 90°. The ester is soluble in sodium carbonate solution, from which it is precipitated by acids; hydrolysis in cold alkaline solution leads to the production of *trimethylacetylpyruvic acid*, $C_8H_{12}O_4$, m. p. 60°. No evidence has been obtained of the existence of this compound or its ester in the ketonic form. W. O. W.

New Synthetical Passage from the Aliphatic to the Aromatic Series. Telemachos Komnenos (*Monatsh.*, 1910, 31, 135—141).—By the condensation of tetra-acetylethane with succinic acid and acetic anhydride, a compound, $C_{14}H_{16}O_6$, is formed, which has a characteristic aromatic odour and crystallises in large needles, m. p. 60°. It is not an acid, but is unsaturated, forming a bromine additive product, m. p. 72°, from which hydrogen bromide is easily eliminated. Dilute nitric acid oxidises it, yielding oxalic acid. It contains acetyl groups, and after hydrolysis yields a compound, m. p. 178°.

E. F. A.

Lactose and its Behaviour in Aqueous Solutions. Wilhelm Fleischmann and G. Wiegner (*J. Landw.*, 1910, 58, 45—64).—The sp. gr. values obtained by Schmoeger for solutions of lactose up to 36% and those given in the present paper for greater concentrations may be calculated as functions of the concentration x in weights per cent. by the following formula: $D_4^{20} = 0{\cdot}9982 + 3{\cdot}7585x.10^{-3} + 1{\cdot}1284x^2.10^{-5} + 5{\cdot}8405x^3.10^{-8}$.

The formula gives values for D up to 62·05% of crystallised lactose. With concentrations of 11·96%, the D is correctly given by the first three members of the equation.

The probable value for D of pure liquid lactose is $D_4^{20} = 1{\cdot}5453$. When lactose is dissolved in water, a contraction, varying with the

concentration, takes place, being greatest in solutions containing 54·03%, in which the contraction amounts to 0·596 c.c. in 100 grams of solution.

Assuming other constituents of milk to have no effect, the contraction in 100 grams of average milk, due to lactose, will be 0·094 c.c., and will vary between 0·077 and 0·116 c.c.

The results of calculations of the volume of milk from the sum of the volumes of the single constituents make it probable that the sp. gr. of liquid proteins is about D_{15}^{15} 1·46. N. H. J. M.

Some Kinds of Gums. Ernst Meininger (*Arch. Pharm.*, 1910, 248, 171—201).—Gums obtained from various species of Acacia grown in known localities have been examined. The gum from *Acacia pycnantha*, grown in Victoria and South Australia, contains 13·55% of moisture, 0·92% ash (0·28% being calcium and 0·123% magnesium), 0·64% of matter insoluble in water; the aqueous solution has an acid reaction, does not reduce Fehling's solution, and has α_D −19·39° (p = 7·9992 and D = 1·0325). The arabic acid, that is, the organic part remaining after the removal of the inorganic constituents, contains 1·31% of nitrogen, whereas the unpurified dried gum contains 2·19%. The dried gum yields a yellow, amorphous *acetyl* derivative by treatment with acetic anhydride and sodium acetate at 110—120°. By oxidation with nitric acid, D 1·15, the gum yields an amount of mucic acid corresponding with 58·61% of galactan, whilst the furfuraldehyde and methylfurfuraldehyde obtained by distilling the gum with 12% hydrochloric acid represent 16·98% of pentosan and 2·92% of methylpentosan respectively. Hydrolysis of the gum by dilute sulphuric acid yields *d*-galactose and *l*-arabinose.

The gum from *Acacia horrida*, grown in South and South-West Africa, contains moisture 15·34%, ash 2·59% (Ca 1·06%; Mg 0·345%), matter insoluble in water 0·98%. Its aqueous solution has α_D 53·94° (p = 8·156; D = 1·0342). The acetylated gum is a light brown powder. The arabic acid contains 0·71% of nitrogen, whilst the original gum contains 1·51%. The mucic acid obtained by oxidation represents 27·36% of galactan; the amounts of pentosan and methylpentosan are 36·50 and 2·82% respectively. Hydrolysis of the gum by dilute sulphuric acid yields *l*-arabinose and *d*-galactose.

The gum (Babool gum) from *Acacia arabica*, grown in Africa, Arabia, and India, contains moisture 14·39%, ash 2·41% (Ca 0·765%; Mg 0·106%), and is only partly soluble in water. It contains 50·43% of pentosan and 21·85% of galactan, and yields *l*-arabinose and *d*-galactose by hydrolysis.

The gum from *Melia Azadirachta*, grown in the Deccan, Ceylon, and the Malay Archipelago, contains moisture 15·41%, ash 2·99% (Ca 0·76%; Mg 0·294%), and 0·27% of matter insoluble in water. The aqueous solution has α_D −57·16° (p = 7·958 and D = 1·0332). It contains 11·11% of galactan, 26·27% of pentosan, and yields *l*-arabinose and *d*-galactose by hydrolysis.

The preceding gums respond to Lassaigne's test for nitrogen when potassium is used instead of sodium (compare Stevens, Abstr., 1905, i, 574; Bach, Abstr., 1908, i, 238). C. S.

Conversion of Cellulose into Sugar. Hermann Ost and L. Wilkening (*Chem. Zeit.*, 1910, **34**, 461—462).—The hydrolysis of cellulose by heating in an autoclave with dilute sulphuric acid is unsatisfactory, since at the high temperature necessary, dextrose is in part converted into reversion products and in part into acids and humus substances. Flechsig's method, the conversion of cellulose by cold concentrated sulphuric acid into dextrins and the hydrolysis of these by boiling with dilute acids, has been adversely criticised by Schwalbe and Schulz (this vol., i, 301), but it is now shown that treatment for three hours with 72% sulphuric acid and then for one hour with 2—3% of acid gives almost theoretical yields of dextrose, and after neutralisation and fermentation, over 80% of the theoretical quantity of alcohol. The purity of the dextrose was controlled by the phenylosazone test and by the optical rotatory power. E. F. A.

New Cellulose Derivatives of Low Nitrogen Contents. Jasper E. Crane and Clarence M. Joyce (*J. Soc. Chem. Ind.*, 1910, **29**, 540—542. Compare Hake and Bell, Abstr., 1909, i, 457).—A *product*, $C_{12}H_{21}O_{13}N$, probably $C_{12}H_{19}O_9{\cdot}NO_3,H_2O$, is obtained by the following process. Cellulose, in the form of purified cotton yarn, high grade cotton, tissue paper, or Swedish filter paper, is immersed for a few seconds in a mixture containing 65·5% sulphuric acid, 9% of nitric acid, and 25·5% of water. After removal, the product is drained for twelve minutes at 10°, when it becomes quite gelatinous; it is then plunged into cold water, producing a white, curdy precipitate, which is purified by solution in dilute sodium hydroxide, precipitation by means of hydrochloric acid, and extraction with alcohol and ether or acetone.

It forms a hard, white powder, dissolves in concentrated acids or strong alkalis, in certain phenols, and in Schweitzer's reagent or in zinc chloride solution. The solution in sodium hydroxide, when kept for some time, yields products soluble in water. The nitrocellulose reacts vigorously with acetic anhydride and a little water, yielding an *acetyl* derivative, $C_{22}H_{31}O_{18}N$, which dissolves readily in acetone.

The compound obtained is the lowest cellulose nitrate yet prepared, and in properties resembles cellulose hydrates rather than the nitrates.

A brief summary of the products formed by the action of concentrated sulphuric acid, concentrated nitric acid, and of dilute acids is given. The conclusion is drawn that the important factor in the action of acids is the percentage of water in the acid. With 20—40% of water, hydrates are formed, but with 50—60% of water, hydrolysis occurs and hydrocelluloses are formed. With the mixed acids each acid endeavours to carry out its characteristic function, and at the same time the water present tends to hydration or hydrolysis, according to the amount present. The formation of the nitrate described above is due to the sulphuric acid dissolving the cellulose, forming sulphuric esters, which are decomposed by the water to cellulose hydrates, and these in their turn are converted into nitrates.

J. J. S.

Platinichlorides and Periodides of Di- and Tri-methylamine and their Employment in the Separation of the Bases. Jean Bertheaume (*Compt. rend.*, 1910, **150**, 1063—1065).—Details are given of the solubility in alcohol of the platinichlorides of di- and tri-methylamine at different temperatures. The small difference in solubility of these salts renders useless the methods proposed by Bresler (*Ann. Chim. anal.*, 1901, [vi], 28) and Eisenberg (Abstr., 1881, 246) for separating the bases. For the same reason the method of Weiss (*Annalen*, 1892, **267**, 258), based on differences in the solubility of the periodides, is said to be unsatisfactory.

Dimethylamine periodide, $NHMe_2,HI,I_3$, is stable, and crystallises in hexagonal tablets, m. p. 83—85°; like the corresponding trimethyl-compound, its solubility is considerably lowered by the presence of magnesium sulphate or of alkali chlorides. W. O. W.

Compounds of Hexamethylenetetramine with Mercuric Salts. Ed. Schmiz (*Ber. deut. Pharm. Ges.*, 1910, **20**, 201—202).—In extension of the work of Grishkewitsch-Trochimowsky (this vol., i, 108) and Riedel (D.R.-P. 217897), the author describes additive products of this amine with mercuric chloride, iodide, and sulphate, formed by mixing dilute solutions of the amine and the salt in each case.

The *mercuric chloride* compound, $C_6H_{12}N_4,2HgCl_2$, crystallises in colourless needles, is sparingly soluble in water, more so on addition of ammonium chloride, decomposes when heated in water at 80°, and evolves formaldehyde when warmed with dilute sulphuric acid.

The *mercuric iodide* compound, $C_6H_{12}N_4,2HgI_2$, forms small yellowish-white needles, and the *mercuric sulphate* compound, of analogous composition, occurs in colourless, silky needles. T. A. H.

Compounds of Amino-acids and Ammonia. V. Peter Bergell and Hanns von Wulfing (*Zeitsch. physiol. Chem.*, 1910, **65**, 489—496. Compare this vol., i, 304).—*Chloroacetyl-leucinamide*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

obtained from chloroacetyl chloride, leucinamide hydrobromide, and alkali, crystallises from dilute alcohol in nacreous plates, m. p. 157° (corr.), and when shaken for six hours with 25% aqueous ammonia and the mixture kept for twelve hours at 40°, yields *glycyl-d-l-leucinamide*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO\cdot NH_2)\cdot CH_2\cdot CHMe_2$, as the *hydrochloride*, which crystallises in minute plates, m. p. 211—212° (corr.)

Bromopropionyl-leucinamide,

$$CHMeBr\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

obtained by the action of bromopropionyl bromide on leucinamide hydrobromide and alkali, crystallises in slender needles, m. p. 150—151° (corr.), and with ammonia yields *alanyl leucinamide hydrobromide*,

$$HBr,NH_2\cdot CHMe\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

which melts at 140° when anhydrous.

Chloroacetylglycyl-leucinamide,

$$CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

obtained from glycyl-leucinamide hydrochloride and chloroacetyl chloride, crystallises in minute needles, m. p. 190—191° (corr.).

In many of these preparations it is not necessary to isolate the amino-compound in the pure state; for example, for the preparation of chloroacetyl-leucinamide, it is merely necessary to heat bromo*iso*-hexoamide with alcoholic ammonia at 105—110°, to evaporate under reduced pressure, extract the residue with a little water, and to treat the clear aqueous solution with chloroacetyl chloride and alkali.

The chloroacetyl derivatives are of use in detecting amides of amino-acids and peptides. J. J. S.

Behaviour of Racemic Aspartic Acid on Putrefaction. Carl Neuberg (*Archiv. Fisiol.*, 1909, 7, 87—90).—By ordinary putrefactive bacteria, inactive aspartic acid was not decomposed into optically active components. W. D. H.

The *cyclo*Octane Series. IV. Richard Willstätter and Ernst Waser (*Ber.*, 1910, 43, 1176—1183).—The authors have undertaken the preparation of *cyclo*octene, which is an important member of this group (compare Harries, Abstr., 1907, i, 35), by the method of reduction with platinum-black previously employed (Abstr., 1908, i, 383, 636), and they have used the same means to obtain tropane and α-dimethylaminopentane.

Δ^4-*des*-Dimethylgranatanine, $C_8H_{13}NMe_2$ (compare Willstätter and Veraguth, Abstr., 1905, i, 515, 543), has b. p. 80°/9 mm., 95°/19 mm., or 210—210·5°/760 mm., and d_4^0 0·910 (rather lower than formerly given). On shaking this substance for at least a day with platinum-black in an atmosphere of hydrogen, *dimethylamino*cyclo*octane* was obtained as a mobile oil, b. p. 86—86·5°/11 mm., or 216—217°/760 mm. It has d_4^0 0·900, d_4^{20} 0·883, n_D^{20} 1·4790. Its *platinichloride* has m. p. 183—184°, and the *methiodide*, 270—271° (decomp.). On distilling the *quaternary ammonium hydroxide* (from the above methiodide), cyclo*octene* is produced, b. p. 143·5°/730 mm. (corr. 145°). It has d_4^0 0·871, d_4^{20} 0·855, n_D^{20} 1·4739. The substance polymerises easily.

*Bromo*cyclo*octane*, $C_8H_{15}Br$, is formed quantitatively from *cyclo*octene and hydrobromic acid in glacial acetic acid. It is an oil, b. p. 90·5—91·5°/10 mm. It has d_4^0 1·309, d_4^{20} 1·290, n_D^{20} 1·5112, and yields with magnesium and carbon dioxide a cyclo*octanecarboxylic acid*, which is being investigated. cyclo*Octane*, C_8H_{16}, is obtained by reducing *cyclo*octene, as above described, in purer form than by the method formerly employed (Willstätter and Veraguth, Abstr., 1907, i, 303), and has b. p. 147·3—148·3°/709 mm. (corr. 149·6—150·6°), m. p. 14·2—14·4°, d_4^{20} 0·839, n_D^{20} 1·4586.

By reducing tropidine in the same way, tropane is readily prepared. It has b. p. 163—165° (corr.).

α-*Dimethylaminopentane* (from dimethylpiperidine) has b. p. 122—123° (corr.), d_4^0 0·755, d_4^{20} 0·743, n_D^{20} 1·4083. The *platinichloride* has m. p. 127—128°, and the *methiodide*, m. p. 222—223°.

R. V. S.

Δ^3-*cyclo*Hexene Derivatives. W. Sobecki (*Ber.*, 1910, 43, 1038—1041).—When potassium phthalimide is heated for six to

eight hours at 180—190° with 1 : 4-dibromo*cyclo*hexane, substituted derivatives of *cyclo*hexane are not obtained, but hydrogen bromide is eliminated and phthalimide and Δ^3-bromo*cyclo*hexene are formed. When the dibromo-derivative is heated with quinoline, the chief product is *cyclo*hexadiene.

Δ^3-*Bromocyclohexene*, C_6H_9Br, is a colourless, highly refractive liquid, with b. p. 54—54·5°/15 mm., and D_4^{15} 1·3772. It distils at 160—163° under atmospheric pressure, but is partly decomposed. It has an odour of allyl bromide, and turns brown when kept for several weeks. With alcohol and concentrated sulphuric acid it gives an intense red coloration. The *dibromide*, $C_6H_9Br_3$, is an oil. The bromo*cyclo*hexene forms a Grignard compound, and this reacts with carbon dioxide, yielding Δ^3-*cyclo*hexenoic acid (W. H. Perkin, Trans., 1904, **85**, 431).

A small yield of Δ^3-cyclo*hexenaldehyde*, $C_7H_{10}O$, can be obtained by the action of ethyl orthoformate on the Grignard compound from Δ^3-bromo*cyclo*hexene in the presence of dry toluene, and subsequent hydrolysis of the acetal. It has b. p. 58°/17 mm. and D_4^{15} 0·9524; it is characterised by an extremely disagreeable odour, readily polymerises, and yields a *semicarbazone*, $C_8H_{13}ON_3$, m. p. 153·5—154·5°.

J. J. S.

Some Hydrocarbons of the Diphenyl Series. Erling Schreiner (*J. pr. Chem.*, 1910, [ii], **81**, 422—424).—The following hydrocarbons have been prepared by heating iodo-compounds with "Naturkupfer" (copper bronze) in a glass flask : 4 : 4′-*Diethyldiphenyl*, $C_6H_4Et{\cdot}C_6H_4Et$, m. p. 80°, from *p*-iodoethylbenzene ; 4 : 4′-*diisopropyldiphenyl*, m. p. 49°, from *p*-iodo*iso*propylbenzene ; 4 : 4′-*di*tert.-*butyldiphenyl*, m. p. 122°, from *p*-iodo*tert.*-butylbenzene. All three are colourless, crystalline substances.

C. S.

Hydrocarbons from ω-Bromostyrene and Preparation of γ-Phenylbutyric Acid. Hans Rupe and H. Proske (*Ber.*, 1910, **43**, 1231—1234).—Rupe and Bürgin (this vol., i, 161) have shown that by the action of magnesium on cinnamyl chloride, a branched-chain hydrocarbon, α,δ-diphenyl-Δ^{α}-hexene, is the main product.

By the action of magnesium on ω-bromostyrene, the main product is styrene, but a certain amount of the normal magnesium halogen compound interacts with a second molecule of bromostyrene, forming αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene, $CHPh{:}CH{\cdot}CH{:}CHPh$, crystallising in nacreous plates, m. p. 147—148°.

Phenylbutyric acid is readily obtained by the interaction of γ-bromo-α phenylpropane and magnesium in ether, saturation with carbon dioxide, and subsequent hydrolysis ; it crystallises in colourless, fatty, lustrous plates, m. p. 52°.

E. F. A.

Triphenylmethyl, Triphenylacetaldehyde, and Triphenylacetic Anhydride. Julius Schmidlin (*Ber.*, 1910, **43**, 1137—1144). —Triphenylacetyl chloride (Schmidlin and Hodgson, Abstr., 1908, i, 170) when treated with magnesium phenyl iodide does not yield

β-benzopinacolin, as would be expected, but carbon monoxide is split off and triphenylmethyl is formed. The triphenylmethyl is isolated from ethereal solution in crystals containing ether of crystallisation. The substance has the formula $2CPh_3,Et_2O$, and m. p. 85—90° (with liberation of ether). Only in one experiment was a trace of β-benzopinacolin produced. When the reaction is carried out at the b. p. of ether, triphenylcarbinol and triphenylmethane are obtained. The removal of carbon monoxide from triphenylacetyl chloride is also effected by molecular silver; a small quantity of triphenylacetic anhydride may be formed as a by-product.

The Grignard reaction with triphenylacetyl chloride proceeds normally when, instead of the iodide, magnesium phenyl bromide is employed. β-Benzopinacolin is obtained, and no trace of carbon monoxide is evolved. The author finds other instances of this difference between iodide and bromide (compare following abstract). *p*-Benzoyltriphenylmethane reacts with magnesium phenyl bromide, but not with the iodide. Whilst magnesium phenyl bromide and ω-chlorotriphenylmethane yield tetraphenylmethane (Gomberg, Abstr., 1906, i, 414; Freund, Abstr., 1906, i, 574), the action of magnesium phenyl iodide on ω-chlorotriphenylmethane yields triphenylmethyl (which may be prepared in this way) according to the equation: $CPh_3Cl + 2PhMgI = 2CPh_3 + Ph_2 + 2MgICl$. The production of diphenyl was observed.

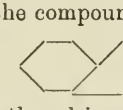
The action of magnesium ethyl iodide on triphenylacetyl chloride yields *triphenylmethyl ethyl ketone*, m. p. 103—104° (corr.).

Triphenylacetic anhydride, prepared from *silver triphenylacetate* and triphenylacetyl chloride, has m. p. 163° (corr.), with effervescence due to splitting off of carbon monoxide. It is hydrolysed with difficulty.

Magnesium triphenylmethyl chloride reacts with ethyl formate, yielding *triphenylacetaldehyde* in small laminæ (from ether), m. p. 223·5° (corr.), with development of a red coloration and evolution of carbon monoxide. The mother liquors contain a *substance* which, with concentrated sulphuric acid, gives an intense bluish-green coloration, becoming red. The aldehyde, like diphenylacetaldehyde (Breuer and Zincke, Abstr., 1880, 118), cannot be oxidised to the corresponding acid. R. V. S.

Pentaphenylethanol. Julius Schmidlin and Julius Wohl (*Ber.*, 1910, 43, 1145—1152).—The preparation of this compound has been effected from β-benzopinacolin and magnesium phenyl iodide, although the use of the bromide is impossible for this purpose (compare Gomberg, Abstr., 1906, i, 414; also Abstr., 1907, i, 27, and preceding abstract). For the reaction a large excess (7—8 molecules) of the iodide must be taken, and solution only takes place after boiling has been continued for twenty hours. The raw product is purified by means of light petroleum, and recrystallised from ether and from benzene. Pure *pentaphenylethanol* forms colourless prisms, m. p. 179° (corr.), and remains unaltered when kept for some time at the m. p. Impure specimens gradually decompose when kept for a long time at the ordinary temperature. On distillation in a vacuum the

substance yields triphenylmethane. The hydroxyl group does not condense with amines or phenols, and cannot be replaced. On heating the compound with very concentrated hydrobromic acid, halogen is introduced, but without replacing the hydroxyl group. Hydrochloric acid, acetyl chloride, and phosphorus pentachloride all yield a stable substance, *dehydropentaphenylethanol*, containing two hydrogen atoms less in the molecule. The same substance is found in the mother liquors in the preparation of pentaphenylethanol. It forms hard, lustrous crystals, m. p. 188° (corr.), and gives a green coloration with sulphuric acid. On oxidation β-benzopinacolin is formed, and hence the authors ascribe to the compound the constitution:



Dehydropentaphenylethanol is converted by sulphuric acid into an isomeride, iso*dehydropentaphenylethanol*, which crystallises with 1½ molecules of benzene of crystallisation in short, thick prisms, m. p. 238° (corr.), the benzene being evolved previously at a much lower temperature. This isomeride is also formed when pentaphenylethanol is shaken in benzene solution with sulphuric acid.

When triphenylmethyl peroxide is distilled in a vacuum, the distillate contains phenol, whilst the residue consists chiefly of tetraphenylethylene; triphenylmethane was not found to be present.

Further investigation of the substance formerly (*loc. cit.*) described as being possibly hexaphenylethane containing admixed magnesium has not justified that supposition. R. V. S.

αβ-Dichlorotetraphenylethane, the Chlorine Derivative of α-Benzopinacolin. Julius Schmidlin and Robert von Escher (*Ber.*, 1910, **43**, 1153—1161).—When diphenyldichloromethane (from benzophenone) is shaken for a long time (thirty-six hours) with molecular silver (1 molecule), *αβ-dichloro-s-tetraphenylethane* is produced. The liquid must be kept homogeneous by shaking until the reaction is complete, otherwise only tetraphenylethylene and unchanged diphenyldichloromethane are obtained. αβ-Dichloro-*s*-tetraphenylethane has m. p. 186° (corr.), with evolution of hydrogen chloride. It forms crystals containing one molecule of benzene of crystallisation. It is soluble in concentrated sulphuric acid and in cold acetic acid, but when boiled with the latter, hydrogen chloride is evolved, with formation of a monochloride. Boiling water also causes chlorine to split off, yielding α-benzopinacolin, but no reaction takes place with moist silver oxide or with silver acetate. The action of silver on αβ-dichloro-*s*-tetraphenylethane leads to the production of tetraphenylethylene, which is also formed when the substance is distilled, and when it is acted on by aliphatic or aromatic Grignard solutions or by phenylhydrazine. With benzene and aluminium chloride, an unusual reaction occurs, 9 : 10-diphenylphenanthrene (compare Werner and Grob, Abstr., 1904, i, 864) being produced. The monochloro-compound also yields 9 : 10-diphenylphenanthrene under these conditions.

The constitution of the *monochloro*-compound, $C_{26}H_{19}Cl$, obtained

from tetraphenyldichloroethane as above-mentioned, has not been settled. It has m. p. 187° (corr.), without evolution of gas, and on boiling with water no chlorine is evolved. The compound could not be obtained free from *a*-benzopinacolin. *αβ*-Dichlorotetraphenylethane when heated with phenol also gives this monochloro-compound, whilst with aniline a small amount of a hydrocarbon was obtained in glittering, green needles, m. p. 145°. R. V. S.

Perchloric Acid as a Reagent in Organic Chemistry. Karl A. Hofmann, August Metzler, and Kurt Höbold (*Ber.*, 1910, 43, 1080—1086).—Perchlorates possess many advantages over picrates for the separation of carbinols, ketones, and amines in a state of purity. They are obtained by treating solutions in ether, benzene, tetrachloroethane, or carbon tetrachloride with 70% perchloric acid, or even using the concentrated acid alone or mixed with acetic acid as solvent. As a class they crystallise well and are not dangerous. To eliminate the perchloric acid, it suffices to wash feebly basic substances with water, or strongly basic substances are shaken with potassium carbonate or calcium oxide in a suitable solvent. They are analysed by fusing with sodium carbonate in a platinum crucible and estimating the chlorine.

Coerulignone diperchlorate forms green, glistening, dark blue crystals. *Gallein perchlorate* crystallises in lancet-shaped plates of a metallic green lustre, but red in transmitted light; it is doubly refractive, and yields a red ethereal solution.

Isatin perchlorate forms yellow or almost colourless, four-cornered, obliquely-cut prisms. Indigotin yields a *perchlorate* in the form of a bluish-black powder.

α-Methylindole perchlorate separates in flat, colourless, lustrous prisms, decomp. 170°.

Acridine perchlorate crystallises from glacial acetic acid in thick, four-cornered, yellow prisms, or from carbon tetrachloride in greenish-yellow, hexagonal plates.

Phenazine diperchlorate is a deep red, crystalline powder with a bluish reflex; it becomes yellow when exposed to the atmosphere. The colour of this diperchlorate is in marked contrast to that of the simple acid salts of phenazine.

Azobenzene perchlorate is a yellow powder, consisting of doubly refractive, wine-yellow plates.

Triphenylamine monoperchlorate, $C_{18}H_{15}N,ClO_4H$, forms colourless crystals exploding at 180°. The formation of this salt shows that triphenylamine still has basic properties. *Triphenylamine hemiperchlorate*, $2(C_{18}H_{15}N),ClO_4H$, forms cubical or octahedral crystals of greenish lustre, decomp. 220°. The green coloration is regarded as an impurity. p-*Tritolylamine monoperchlorate* separates in almost colourless, granular crystals, which explode at about 180°; a *hemiperchlorate* forms bright green, lustrous prisms. When a large excess of perchloric acid is used, a *diperchlorate*, $C_{20}H_{21}N,2ClO_4H$, is obtained, crystallising in steel-blue or bluish-green, flat prisms, but this coloration is attributed to associated impurity. Tritolylamine, therefore, has basic properties, and forms normal colourless salts.

Diphenylamine perchlorate separates in clear, colourless, cubical crystals; when exposed to light, it only very slowly becomes faintly blue.

Perchloric acid (70%) has hardly any oxidising action at the ordinary temperature, and does not, for example, affect quinol or trichloroquinone. Chrysene by crystallisation from perchloric acid is obtained in colourless, silver, glistening, irridescent platelets, m. p. 250°.

Diphenylfulvene, dissolved in glacial acetic acid and treated with perchloric acid, forms a bright green powder, possibly the perchlorate, but the original substance is not re-formed on hydrolysis. E. F. A.

Derivatives of Amino-acids. Emil Abderhalden and Paul Blumberg (*Zeitsch. physiol. Chem.*, 1910, 65, 318—322).—The authors have investigated the compounds formed by the action of chlorodinitrobenzene on amino-acids, in the hope of discovering substances which would facilitate the isolation of the latter from urine. The undermentioned compounds, however, crystallise well only when prepared from the pure amino-acids. The reaction is effected by heating together for two hours an aqueous solution of 1 molecule of amino-acid and 2 molecules of sodium hydrogen carbonate, and an alcoholic solution containing 1 molecule of chlorodinitrobenzene. After evaporation, the residue is dissolved in water, and precipitated with hydrochloric acid, the product being recrystallised from acetic acid and water. 2 : 4-*Dinitrophenylglycine* forms golden crystals, m. p. 205°, the yield being 70%. 2 : 4-*Dinitrophenylglycine ethyl* ester crystallises in greenish-yellow needles, m. p. 144°; yield 85%. 2 : 4-*Dinitrophenyl*-dl-*alanine* forms small, golden laminæ, m. p. 178°; yield 60%. 2 : 4-*Dinitrophenyl*-dl-*valine* also crystallises in golden laminæ, m. p. 185° (previously sintering); the yield is 85%. 2 : 4-*Dinitrophenyl*-dl-*leucine* forms yellow crystals with a greenish lustre, m. p. 203° (with production of a red coloration). 2 : 4-*Dinitrophenylasparagine* has m. p. 191—192°; yield 60%.

With histidine two derivatives are obtained. *Mono*-2 : 4-*dinitrophenylhistidine* crystallises in long, red needles. *Di*-2 : 4-*dinitrophenylhistidine* forms greenish-yellow crystals, which decompose at 250°. 2 : 4-*Dinitrophenyl*-dl-*leucine* crystallises in greenish-yellow laminæ, m. p. 169° (previously sintering); yield 60%. R. V. S.

Preparation of 5-Halogen-6-chloro-2-acylaminotoluenes. Badische Anilin- & Soda-Fabrik (D.R.-P. 217896).—The halogenation in a convenient solvent of 6-chloro-2-acyltoluidines with either chlorine or bromine yields compounds which contain the second halogen atom in the para-position to the acylamino-group. The preparation of 5 : 6-*dichloroaceto-o-toluidide*, needles, m. p. 144—145°, and of 6-*chloro*-5-*bromoaceto-o-toluidide*, m. p. 154—155°, is described in the patent. F. M. G. M.

[**Preparation of 3-Chloro-o-toluidine-5-sulphonic Acid.**] Badische Anilin- & Soda-Fabrik (D.R.-P. 218370).—3-*Chloro*-o-*toluidine*-5-*sulphonic acid* is prepared by treating 2-acylamino-5-toluenesulphonic acids in aqueous solution with chlorine and subsequent

hydrolysis of the acyl group; it forms needles which are readily soluble in hot water; by heating with 75% sulphuric acid at 150—160°, the sulphonic group is removed, yielding 3-chloro-*o*-toluidine.

F. M. G. M.

Preparation of Optically Inactive *o*-Dihydroxyphenylalkylamines. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 220355).—The synthetic *o*-dihydroxyphenylalkylamines are optically inactive, and their resolution into the required components is important, as, contrary to the opinion generally held, the dextro-compounds possess valuable therapeutic properties.

It is found that both the dextro- and the lævo-compound can be racemised by treatment with sulphuric or hydrochloric acid; the inactive mixture is then resolved into the active components, and the isomeride which is not required again racemised and subsequently resolved, the process being repeated indefinitely. Examples are given of the racemisation of *l*-*o*-dihydroxyphenylethanolmethylamine (*l*-adrenaline), α_D −50°, of *d*-adrenaline, and of natural *l*-adrenaline, in which the base is treated with 1·5 mols. of hydrochloric acid in water and the temperature maintained at 80—90° during several hours.

F. M. G. M.

Influence of Constitution on the Velocity of Decomposition of Quaternary Ammonium Salts. Edgar Wedekind and F. Paschke (*Ber.*, 1910, **43**, 1303—1312. Compare Abstr., 1906, i, 14, 161, 419; also Halban, Abstr., 1907, ii, 246; 1908, i, 627).—A comparison of the rates of racemisation of the isomeric *l*-phenylbenzylmethyl-*n*-butylammonium iodide and *l*-phenylbenzylmethyl*iso*butylammonium iodide in chloroform solution at 25° shows that the *iso*-butyl derivative is racemised about four times as quickly as its isomeride.

The rates of decomposition of a number of quaternary ammonium salts into tertiary amine and alkyl halide have been determined in dilute (1—2%) chloroform solution at 35° and 45°. The method adopted was, at the end of given periods of time, to extract the chloroform solution (5 or 10 c.c.) twice with 125 c.c. of water, to mix the two aqueous extracts, and titrate with silver nitrate according to Volhard's method. The water extracts the ionised ammonium salts, whereas the products of decomposition are retained by the chloroform. The addition of alcohol, as recommended by von Halban, is not advisable, as it lowers the rate of dissociation. The following salts are quite stable in dilute chloroform solution, namely: tetraethyl-, triethylallyl-, benzyltriethyl-, and methyldiethyl-phenylammonium iodide. For other salts the following constants were obtained:

	K.	
	35°	45°
Phenylbenzyldiethylammonium bromide	$1·7 \times 10^{-3}$	$6·5 \times 10^{-3}$
Phenylbenzyldimethylammonium bromide		$1·3 \times 10^{-3}$
Phenylbenzyldiethylammonium iodide	$9·9 \times 10^{-3}$	$3·5 \times 10^{-2}$
Phenyldibenzylmethylammonium iodide	$5·3 \times 10^{-3}$	
Phenyldiethylallylammonium iodide	$4·1 \times 10^{-4}$	$1·6 \times 10^{-3}$

It is thus clear that only those salts undergo measurable decomposition which contain both a phenyl group and also an unsaturated group, such as benzyl or allyl.

Of the phenylbenzyldialkylammonium salts, the dimethyl is the most stable, the replacement of one methyl group by a propyl, *n*-butyl, or an allyl group doubles the value of K, and the replacement of two methyl by two ethyl groups increases K in the ratio 1 : 5.

The decomposition of phenylbenzyldiethylammonium bromide in chloroform solution has been studied in detail, and the conclusion is drawn that the products of dissociation are diethylaniline and benzyl bromide.

It is pointed out that those salts which are most readily dissociated in chloroform solution are the salts which are most readily resolved into their optically active components.

Methylallyltetrahydroquinolinium iodide (Abstr., 1907, i, 1073), which racemises extremely readily in methyl alcoholic solution, appears to undergo but slight dissociation in the same solvent. J. J. S.

Replacement of Halogen by the Nitro-group. I. L. Chas. Raiford and Frederick W. Heyl (*Amer. Chem. J.*, 1910, 43, 393—398).—It has been shown by Armstrong and Harrow (Abstr., 1876, i, 477) that nitric acid reacts with 2 : 4 : 6-tribromophenol with formation of 2 : 6-dibromo-4-nitrophenol. Claus and Hirsch (Abstr., 1889, 389) found that 2 : 4 : 6-tribromo-*m*-cresol is similarly converted into 2 : 6-dibromo-4-nitro-*m*-cresol, whilst by the action of nitrous acid on the same tribromo-compound, Zincke (Abstr., 1900, i, 545) also obtained a dibromo-4-nitro-*m*-cresol.

On repeating Zincke's work at 12—15°, a mixture of two nitro-derivatives has been obtained, in which the nitro-groups are in the ortho- and para-positions respectively to the hydroxyl group.

When sodium nitrite is added gradually to a solution of 2 : 4 : 6-tribromophenol in glacial acetic acid at 12—15°, a mixture of 4 : 6-dibromo-2-nitrophenol, m. p. 117°, and 2 : 6-dibromo-4-nitrophenol, m. p. 141°, is obtained. 2 : 4 : 6-Trichlorophenol does not react with nitrous acid under these conditions. E. G.

Preparation of Glycerol Mono-*o*- and -*p*-chlorophenyl Ethers. Les Etablissements Poulenc Frères and Ernest Fourneau (D.R.-P. 219325).—The chlorophenyl glycerol ethers,

$$C_6H_4\cdot Cl\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

prepared from glycerol monochlorohydrin and the alkali salts of *o*- or *p*-chlorophenol, have valuable therapeutic properties, being tasteless and odourless, whereas the corresponding glycerol phenyl ethers have a bitter taste in aqueous solution.

Glycerol p-*chlorophenyl ether* crystallises from a mixture of ether and petroleum in colourless needles, m. p. 80°, b. p. 214—215°/19 mm.

Glycerol o-*chlorophenyl ether* has m. p. 65°, and b. p. 250°/19 mm. F. M. G. M.

[Preparation of Amino-derivatives of Aromatic Ethers.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 220722. Compare this vol., i, 312).—A description of the preparation of dyes

from diazotised aromatic amino-ethers coupled with pyrazolonesulphonic acids, and naphthylpyrazolonesulphonic acids.

The following new ethers are described :

2-*Aminophenyl* o-*tolyl ether*, a yellow oil, b. p. 196°/23 mm. ; it does not solidify at −13°.

2-*Aminophenyl* m-*tolyl ether*, a colourless, slowly crystallising oil, b. p. 204°/34 mm., m. p. 30°.

2-*Aminophenyl* p-*tolyl ether*, yellow oil, b. p. 193°/20 mm., does not solidify at −13°.

4-*Aminophenyl* o-*tolyl ether*, colourless crystals, m. p. 62°.

4-*Aminophenyl* m-*tolyl ether*, m. p. 79°.

4-*Aminophenyl* p-*tolyl ether*, colourless needles, m. p. 121·5°.

2-*Amino*-4-*sulphophenyl* o-*tolyl ether*, prepared from *o*-chloronitrobenzenesulphonic acid and *o*-cresol ; the free acid is insoluble in water and alcohol ; the *barium* salt forms colourless leaflets.

F. M. G. M.

Action of Sulphur and Selenium on Magnesium *cyclo*Hexyl Chloride. Alphonse Mailhe and M. Murat (*Bull. Soc. chim.*, 1910, [iv], 7, 288—291).—The action of precipitated sulphur on magnesium *cyclo*hexyl chloride is analogous with that on organo-magnesium haloids in general (Wuyts, Abstr., 1909, i, 380).

cyclo*Hexyl mercaptan*, D^0 0·9905, D^{20} 0·9782, n_D 1·481, b. p. 150—152°/152 mm., is the chief product ; it is a colourless liquid of unpleasant alliaceous odour, and furnishes with solutions of metallic salts, *mercaptides* of the general formula $C_6H_{11}SM'$, which are usually different in colour from the corresponding metallic sulphides. Phosphoric acid or anhydride decomposes the mercaptan, forming *cyclo*hexene. On heating in a reflux apparatus with acetic acid, the mercaptan is slowly decomposed, with the formation of hydrogen sulphide and *cyclo*hexyl acetate. On oxidation by dilute nitric acid or chromic acid, or by the action of iodine on the sodium derivative of the mercaptan, cyclo*hexyl disulphide*, $(C_6H_{11})_2S_2$, b. p. 288°, is formed.

Selenium acts on magnesium *cyclo*hexyl chloride in an analogous manner, forming the corresponding *selenol*, $C_6H_{11}\cdot SeH$, D^0 1·1223, b. p. 170—172°, which closely resembles the thiol in properties, and furnishes with metallic salts, metallic *derivatives* of the general formula $C_6H_{11}SeM'$, which are generally of the same colour, but darker than the corresponding mercaptides. No diselenide could be obtained by oxidation of the selenol.

The fact that *cyclo*hexanol has a boiling point intermediate between those of the thiol and the selenol indicates that its molecule is polymerised, since normally it should boil below the thiol.

T. A. H.

Phenolic Ethers Containing the ψ-Allyl Side-chain, $CMe{:}CH_2$. *o*-Hydroxytoluic Series. IV. Auguste Béhal and Marc Tiffeneau (*Bull. Soc. chim.*, 1910, [iv], 7, 330—332).—The anomalous physical properties of certain of the *o*-hydroxytoluic derivatives described in a previous paper (Abstr., 1908, i, 630) have led the

authors to repeat their work, and the following new constants are given for the compounds.

Methyl *o*-hydroxytoluate (m. p. 0°) gives with magnesium methyl iodide, 3-*ψ*-allyl-*o*-cresol, D^0 0·9952, b. p. 100—102°/14 mm. or 211—213°/760 mm., which colours ferric chloride solution orange-red. Its methyl ether has D^0 0·972 and b. p. 208—210°, and is readily reduced by sodium in alcohol, giving *o*-thymyl methyl ether, D^0 0·9518, b. p. 210—212°, and this on demethylation gives *o*-thymol (*iso*thymol), D^0 1·9924 (see succeeding abstract), b. p. 225—226°, which colours ferric chloride orange-yellow, and with sodium and chloroacetic acid furnishes *o-thymyloxyacetic acid*, m. p. 84°. The different physical properties previously ascribed were due to the use of *o*-hydroxytoluic acid containing the *m*-isomeride. T. A. H.

Two New Isomerides of Thymol. 2-Hydroxy-1-methyl-3-*iso*propylbenzene (*o*-Thymol) and 4-Hydroxy-1-methyl-3-*iso*propylbenzene (*p*-Thymol). G. Guillaumin (*Bull. Soc. chim.*, 1910, [iv], 7, 332—342).—The author has applied Béhal and Tiffeneau's method of synthesis (Abstr., 1908, i, 630) to *o*- and *p*-hydroxytoluic acids, and obtained in this way *o*- and *p*-thymols, isomeric with ordinary *m*-thymol already synthesised in like manner from *m*-hydroxytoluic acid (*loc. cit.*).

Methyl o-*methoxytoluate*, $OMe\cdot C_6H_3Me\cdot CO_2Me(2:1:3)$, D^0 1·1258, $D^{17\cdot4}$ 1·1102, $n_D^{17\cdot4}$ 1·51664, b. p. 249·5—250·5°/763 mm. (corr.) or 129—131°/14 mm. (corr.), is a limpid, almost colourless liquid, which with magnesium methyl iodide furnishes the corresponding *tertiary alcohol*, $OMe\cdot C_6H_3Me\cdot CMe_2\cdot OH(2:1:3)$, D^0 1·0542, $D^{14\cdot8}$ 1·0420, $n_D^{14\cdot8}$ 1·52147, b. p. 131—132°/14 mm. (corr.) or 239—243°/760 mm. (decomp.), a pleasant smelling, thick liquid, that on dehydration by hot acetic anhydride gives 2-*methoxy*-1-*methyl*-3-*ψ*-*allylbenzene*, D^0 0·9713, D^{15} 0·9599, n_D^{15} 1·52049, b. p. 96—99°/14 mm. (corr.) or 209—210°/762 mm. (corr.), a colourless, mobile, pungent-smelling liquid. On reduction this furnishes 2-methoxy-1-methyl-3-*iso*propylbenzene (*o*-thymyl methyl ether), D^0 0·9515, $D^{14\cdot6}$ 0·9397, $n_D^{14\cdot6}$ 1·50063, b. p. 210—211°/760 mm. (corr.), a colourless, pleasant smelling liquid (compare Béhal and Tiffeneau, preceding abstract). On demethylation it yields 2-hydroxy-1-methyl-3-*iso*propylbenzene (*o*-thymol), D^0 0·9986, $D_D^{15\cdot2}$ 0·9865, $n_D^{15\cdot2}$ 1·52385, b. p. 225—226°/760 mm. (corr.), a colourless liquid, which becomes green when kept, and has an odour recalling that of *o*-cresol (*loc. cit.*).

3-*Methoxymethyl*-p-*toluic acid*, $OMe\cdot C_6H_3Me\cdot CO_2Me(3:1:4)$, D^0 1·1430, $D^{17\cdot2}$ 1·1287, $n_D^{17\cdot2}$ 1·53016, b. p. 143—146°/14 mm. (corr.) or 263—265°/760 mm. (corr.), is a colourless, almost inodorous liquid. With magnesium methyl iodide it yields the *tertiary alcohol*, $OMe\cdot C_6H_3Me\cdot CMe_2\cdot OH(3:1:4)$, D^0 1·0440, D^{15} 1·0321, n_D^{15} 1·52094, b. p. 134—136°/14 mm. (corr.), which is a viscid, colourless, pleasant-smelling liquid. On dehydration it yields 3-*methoxy*-1-*methyl*-4-*ψ*-*allylbenzene*, D^0 0·9806, $D^{15\cdot8}$ 0·9676, $n_D^{15\cdot8}$ 1·53148, b. p. 105—107°/13 mm. (corr.) or 218—220°/760 mm. (corr.), and this on reduction yields the corresponding 3-*methoxy*-1-*methyl*-4-iso*propylbenzene* (*p*-thymyl methyl ether), D^0 0·9554, $D^{14\cdot8}$ 0·9435, $n_D^{14\cdot8}$ 1·50873, and b. p. 213—214°/760 mm., a

colourless mobile liquid of characteristic odour. On demethylation it yields 3-*hydroxy*-1-*methyl*-4-iso*propylbenzene* (*p*-thymol), D^0 0·9954, $D^{17\cdot8}$ 0·9817, $n_D^{17\cdot8}$ 1·52438, b. p. 228—229°/760 mm. (corr.), m. p. 36°, which is less pungent and more soluble in water than ordinary thymol, and gives no coloration with ferric chloride. Dissolved in acetic acid it gives with sulphuric acid a yellow coloration, whilst the two isomerides give gooseberry-red colorations under these conditions. With chloroacetic acid in presence of sodium hydroxide, it forms p-*thymyl*-3-*oxyacetic acid*, m. p. 131·5°, which occurs in felted masses of crystals, and is slightly soluble in cold water, more so on warming. T. A. H.

Anthranolsulphonic Acids. Carl Liebermann and M. Zsuffa (*Ber.*, 1910, **43**, 1007—1012).—The sodium and potassium salts of the sulphonic acids derived from anthraquinone and its hydroxy-compounds can be reduced by means of tin and concentrated hydrochloric acid in presence of glacial acetic acid to the corresponding sulphonic acids of anthranol and its hydroxy-derivatives. The salts of these reduction products can be readily obtained in a pure form when much acetic acid and only a small amount of concentrated hydrochloric acid is used ; otherwise the products are mixtures of the sulphonic acids, their salts, and alkali chlorides, and the separation is tedious. In certain cases it is not necessary to use hydrochloric acid at all. When the tin is precipitated as sulphide, the greater portion of the sulphonate is carried down at the same time, and can be extracted by means of hot water. The solution is then evaporated under reduced pressure, and the salt crystallises on cooling.

Potassium anthranol-1-*sulphonate*, $C_6H_4<\begin{matrix}CH\text{—}\\ |\\ C(OH)\end{matrix}>C_6H_3\cdot SO_3K$, forms pale yellow plates, and its aqueous solution when made alkaline turns pale orange colour.

Potassium anthranol-1 : 8-*disulphonate*,

$$SO_3K\cdot C_6H_3<\begin{matrix}CH\text{—}\\ |\\ C(OH)\end{matrix}>C_6H_3\cdot SO_3K,$$

forms lemon-yellow, sparingly soluble needles, and yields a red basic potassium salt. The neutral solution yields precipitates with salts of calcium, barium, and lead.

Sodium 1 : 2-*dihydroxyanthranol*-3-*sulphonate*,

$$C_6H_4<\begin{matrix}CH\text{—}\\ |\\ C(OH)\end{matrix}>C_6H_2(OH)_2\cdot SO_3Na,$$

obtained by reducing sodium alizarinsulphonate, is a brilliant yellow salt, and when moist turns brown on exposure to the air. The corresponding *acid*, $C_{14}H_{10}O_6S$, forms pale yellow needles, and is readily soluble.

Sodium 1 : 2 : 6-*trihydroxyanthranolsulphonate*, $C_{14}H_5(OH)_4\cdot SO_3Na$, resembles the 1 : 2-dihydroxy-derivative.

Sodium 1 : 2 : 7-*trihydroxyanthranolsulphonate* crystallises with $2\cdot5H_2O$, which it loses at 110°. The *barium* salt is sparingly soluble.

J. J. S.

Nitroquinol Monomethyl Ether. Hugo Kauffmann and Immanuel Fritz (*Ber.*, 1910, **43**, 1214—1218).—By the hydrolysis of

nitroquinol dimethyl ether, a monomethyl ether was obtained (Abstr., 1907, i, 127), which presented some points of difference from the monomethyl ether described by Weselsky and Benedikt (Abstr., 1881, 1139). It is now shown that both substances are the same.

It would appear that in the dimethyl ether the methoxyl in the ortho-position to the nitro-group is more easily hydrolysed than that in the meta-position. To prove this, it is necessary to show that, on nitration of quinol monoethyl ether, the nitro-group enters into the ortho-position to the free hydroxyl group. Quinol monomethyl ether was coupled with diazotised sulphanilic acid, the dye so formed converted into the benzoyl derivative, and this reduced to *benzoylaminoquinol monomethyl ether*, $OH{\cdot}C_6H_3(OMe){\cdot}NH{\cdot}COPh$. The group $NH{\cdot}COPh$ is here ortho to hydroxyl, as when coupled with quinol monomethyl ether only an ortho-oxyazo-dye is obtained. The same product is obtained on reducing nitroquinol monomethyl ether benzoate.

Nitroquinol monomethyl ether, prepared either by hydrolysis of the dimethyl ether by means of potassium hydroxide dissolved in a mixture of alcohol or water or by the method of Weselsky and Benedikt (*loc. cit.*), forms orange-red crystals, m. p. 80°; the *benzoate* crystallises in lustrous, silky, colourless needles, m. p. 89°.

By the action of nitrous acid on quinol monomethyl ether, *p*-benzoquinone is obtained.

Sodium quinolmonomethyl-ether-azobenzenesulphonate is a red dye; the *benzoate*, prepared by the action of benzoyl chloride in presence of sodium carbonate, forms lustrous, orange-yellow plates, which sinter at 240°, m. p. 260—270° (decomp.).

When reduced with iron and acetic acid, *benzoylaminoquinol monomethyl ether* is obtained as colourless, flat needles, m. p. 160°. The same product is formed on reduction of nitroquinol monomethyl ether benzoate.

The thiocarbamide of aminoquinol dimethyl ether has m. p. 137°, and not 109° as stated by Baessler (Abstr., 1884, 1329). Concentrated hydrochloric acid converts it into 2 : 5-*dimethoxyphenylthiocarbamide*, b. p. 178—180°/16 mm., m. p. 33°. The crystals are almost colourless and do not fluoresce. E. F. A.

Action of Triphenylmethyl on Quinones. Julius Schmidlin, Julius Wohl, and Hans Thommen (*Ber.*, 1910, 43, 1298—1303).—Triphenylmethyl readily combines with *p*-benzoquinone, yielding *quinol triphenylmethyl ether*, $C_6H_4(O{\cdot}CPh_3)_2$, which crystallises in colourless, slender, glistening needles, m. p. 241° (corr.). When heated slightly above its m. p., it turns yellowish-red, but becomes colourless again when cold. When heated for some time above its m. p., the theoretical amount of benzoquinone sublimes. It dissolves in concentrated sulphuric acid, yielding quinol and triphenylcarbinol. The ether is apparently not the first product of the reaction, as a benzene solution of triphenylmethyl turns orange-red on the addition of benzoquinone, but this colour rapidly disappears and the colourless ether is deposited.

The simplest method of obtaining the ether is to shake a benzene

solution of *p*-benzoquinone and triphenylchloromethane with zinc dust during twenty-four hours. It can also be obtained by the action of the *β*-modification of magnesium triphenylmethyl chloride on a benzene solution of benzoquinone.

Similar products have not been obtained by using toluquinone, *o*-benzoquinone, or α-naphthaquinone. *β*-Naphthaquinone gave Stenhouse and Groves' dinaphthyldiquinhydrone (Trans., 1878, **33**, 417).

J. J. S.

Preparation of Hexamethylenetetraminetriguaiacol. F. Hoffmann—La Roche & Co. (D.R.-P. 220267).—*Hexamethylenetetraminetriguaiacol*, $C_6H_{12}N_4,3C_6H_4(OH)\cdot OMe$, is prepared by heating a concentrated aqueous solution of hexamethylenetetramine with guaiacol, or by treating an ammoniacal solution of guaiacol with formaldehyde; the new compound separates from the cooled reaction mixture in long needles, m. p. 80—95°. Boiling with water sets free guaiacol, a reaction which renders this compound a convenient method of keeping guaiacol (m. p. 28°) in a solid condition in tropical climates where the vapour is employed therapeutically. F. M. G. M.

Reduction of Methyl Pulegenate. Hans Rupe and J. Bürgin (*Ber.*, 1910, **43**, 1228—1230).—In continuation of experiments to prepare a high rotatory, optically active primary alcohol (Abstr., 1909, i, 927), methyl pulegenate has been reduced by means of sodium ethoxide to primary *pulegyl alcohol*, $\begin{matrix}CH_2\text{—}CHMe\\ |\\ CH_2\cdot C(CMe_2)\end{matrix}\!\!>\!CH\cdot CH_2\cdot OH$, a viscid, colourless oil, b. p. 105°/10·5 mm., D^{20} 0·9296, n_D^{20} 1·48074, α_D^{20} −1·7°. The alcohol accordingly has only a small rotatory power.

The *acetate* is a mobile, colourless oil of fruity odour, b. p. 110·5—111·5°/9·5 mm.; the *benzoate* is a colourless, viscid, odourless oil, b. p. 186·5—187·5°/9·5 mm. E. F. A.

Action of Organomagnesium Derivatives on Trialkylacetophenones. Mlle. Pauline Lucas (*Compt. rend.*, 1910, **150**, 1058—1061. Compare Haller and Bauer, Abstr., 1909, i, 108, 654).—The action of magnesium methyl iodide on trimethylacetophenone leads to the formation of almost the theoretical amount of *γ-phenyl-ββ-dimethylbutan-γ-ol*, $CMe_3\cdot CMePh\cdot OH$, a viscous liquid, b. p. 116—117°/15 mm., which, on prolonged boiling under ordinary pressure, is partially transformed into an unsaturated *hydrocarbon*, b. p. 88—90°/11 mm., for which the constitution $CMe_3\cdot CPh{:}CH_2$ is suggested.

Magnesium phenyl bromide acts on trimethylacetophenone to give *γγ-diphenyl-ββ-dimethylpropan-γ-ol*, $CMe_3\cdot CPh_2\cdot OH$, b. p. 179—180°/11 mm.; on boiling at the ordinary pressure this loses water, forming an unsaturated *hydrocarbon*, $C_{17}H_{18}$, b. p. 158—159°/11 mm. Under the same conditions, magnesium benzyl chloride furnishes *γδ-diphenyl-ββ-dimethylbutan-γ-ol*, b. p. 175—178°/11 mm.; the corresponding *hydrocarbon*, $C_{18}H_{20}$, has b. p. 164—165°/11 mm., and does not combine with bromine.

Trimethylacetophenone undergoes reduction to γ-phenyl-*ββ*-dimethyl

propan-γ-ol when treated with magnesium propyl iodide; the product was identified by means of its phenylurethane. W. O. W.

Action of Dehydrating Agents on α-Glycols. Marc Tiffeneau (*Compt. rend.*, 1910, **150**, 1181—1184. Compare Abstr., 1907, i, 1035).—On treatment with acetic anhydride, aldehydes of the type CHRR′·CHO give diacetates instead of the expected vinyl acetates. These may be obtained, however, from substituted α-glycols of the type OH·CRR′·CH_2·OH; thus, for example, when estragole glycol is heated for twelve hours with acetic anhydride, a 40% yield of *β*-anisyl-*β*-methylvinyl acetate is produced.

The author declines to admit that the compound obtained by the dehydration of anethole glycol is *β-p*-methoxyphenylpropaldehyde, as stated by Balbiano (Abstr., 1908, i, 901), and adheres to his earlier view (Abstr., 1907, i, 701) that it is identical with anisylacetone. W. O. W.

Isomerism of Some Δγ-Acetylenic Glycols. Georges Dupont (*Compt. rend.*, 1910, **150**, 1121—1123. Compare this vol., i, 85).—The author has discovered fresh instances of isomerism amongst glycols of the type OH·CRR′·C:C·CRR′·OH, a number of which have been described by Iotsitch (*J. Russ. Phys. Chem. Soc.*, 1902, **33**, 242; 1903, **35**, 1269; 1906, **38**, 656). The glycol, *aaaζζζ-hexachloro-Δγ-hexinene-βε-diol*, CCl_3·CH(OH)·C:C·CH(OH)·CCl_3, has been separated by fractional crystallisation from carbon tetrachloride into two isomeric glycols, the less soluble, crystallising in silky needles, m. p. 135°, forms a *diacetate*, m. p. 66—67°, and a *dibenzoate*, m. p. 110—112°, whilst the more soluble isomeride, m. p. 117·5—118°, yields a *diacetate*, m. p. 54—55°, and a *dibenzoate*, m. p. 95—96°. The glycol, *aδ-diphenyl-Δβ-butinene-aδ-diol*, OH·CHPh·C:C·CHPh·OH, similarly exists in two forms; the first, m. p. 142°, is insoluble in ether, forms a *diacetate*, m. p. 88°, and on treatment with bromine furnishes a pasty mass and small quantities of crystals, m. p. 172°; the isomeride, m. p. 103—104°, is soluble in ether, and yields a *diacetate*, m. p. 56—57°, and a *dibromide*, m. p. 182°. The glycol, *βε-diphenyl-Δγ-hexinene-βε-diol*, OH·CMePh·C:C·CMePh·OH, is separable by ether into two compounds; the less soluble has m. p. 163°, whilst the isomeride has m. p. 125—127°; the corresponding *dibromides* have m. p. 124° and 125—127° respectively. W. O. W.

Preparation of Arylsulphoxidoacetic Acids. Farbenwerke vorm. Meister, Lucius & Brüning (D.R.-P. 221261. Compare this vol., i, 320).—The oxidation of arylthioglycol-*o*-carboxylic acids with sodium hypochlorite, also with potassium permanganate, has previously been described.

o-*Chlorophenylsulphoxidcacetic acid*, colourless needles, is obtained when a cold alkaline solution of *o*-chlorophenylthioglycollic acid is treated with chlorine.

p-*Chloro-o-tolylsulphoxidoacetic acid* is analogously prepared, and forms colourless needles. F. M. G. M.

*α-cyclo*Geranic Derivatives. I. Louis Bouveault (*Bull. Soc. chim.*, 1910, [iv], 7, 350—354).—Barbier and Bouveault have shown previously (Abstr., 1897, i, 537) that *cyclo*geranionitrile on hydrolysis furnishes a mixture of two isomeric amides, m. p. 121° and 202° respectively, which cannot be converted into their corresponding acids. It is now shown that the amide, m. p. 121°, corresponds with *α-cyclo*geranic acid, and that the second amide is probably that corresponding with the *β*-acid.

*α-cyclo*Geranic acid was prepared by condensing methylheptenone with ethyl iodoacetate, in presence of zinc and isomerising directly the ethyl geraniate obtained to ethyl *cyclo*geraniate, b. p. 101—102°/10 mm., which was probably a mixture of the *α*- and *β-cyclo*-esters. This was hydrolysed by alcoholic potash at 110—120°, and the acid liberated. The portion which crystallised was collected, and the mother liquors were extracted with ether. The acid so obtained was distilled under reduced pressure and then recrystallised from light petroleum, and yielded pure *α-cyclo*geranic acid, m. p. 106°. This was esterified by heating it with ethyl bromide and sodium ethoxide in alcohol at 120° in a closed vessel. Ethyl *α-cyclo*geraniate, b. p. 101—102°/10 mm., is a colourless liquid, which is saponified with difficulty, yielding pure *α-cyclo*geranic acid. The acid was converted into the chloride by treatment with phosphorus pentachloride, and this on solution in ether and saturation with dry ammonia furnished *α-cyclo*geraniamide, m. p. 120—121°, identical with that obtained from geranionitrile (see above). It is probable therefore that the second amide, m. p. 202°, is *β-cyclo*geraniamide. T. A. H.

*α-cyclo*Geraniol. II. Louis Bouveault (*Bull. Soc. chim.*, 1910, [iv], 7, 354—357).—Ethyl *α-cyclo*geraniate, prepared as described in the preceding abstract, is not reduced by long-continued treatment with sodium in alcohol, indicating that its ethylene linking is in the *βγ*-position. *α*-cyclo*Geranyl acetate*, b. p. 115°/20 mm., obtained by the action of acetic anhydride at 100°, is a colourless liquid. The alcohol also yields a *phenylurethane*, m. p. 75°, which crystallises in colourless needles. When heated with pyruvic acid at 120—140°, *α-cyclo*geraniol furnishes a *substance*, $C_{13}H_{20}O_2$, b. p. 180°/10 mm., m. p. 114°, which crystallises from hot alcohol or a mixture of ether and light petroleum in splendid colourless tablets. It forms crystalline salts with alkalis, but does not combine with bromine or react with hydroxylamine or acetic anhydride. It is possible that a true pyruvate is first formed, and that then a molecule of water becomes attached to the ethylene linking and provokes the formation of a saturated closed-chain with the other end of the pyruvic acid molecule. The formation of this substance is a useful means of identifying *α-cyclo*geraniol. The amide, m. p. 121°, obtained by the hydrolysis of geranionitrile (Abstr., 1897, i, 537), on reduction with sodium in amyl alcohol (Abstr., 1904, i, 213) furnishes *α-cyclo*geraniol, and thus provides further evidence of the derivation of this amide from *α-cyclo*geranic acid (compare preceding abstract).

Commercial *cyclo*geraniol, prepared by the cyclic isomerisation of geranyl acetate, is not homogeneous; it contains *α-cyclo*geraniol, which

was identified by means of the pyruvic acid compound described above, and an isomeric alcohol, yielding a true pyruvate. T. A. H.

Synthesis of *m*-Bromobenzoic Anhydride. Negoita Danaïla (*Bull. Soc. chim.*, 1910, [iv], 7, 286—288).—m-*Bromobenzoic anhydride*, m. p. 148—149°, is prepared by heating at 150—200° during two and a-half hours a mixture of sodium *m*-bromobenzoate and *m*-bromobenzoyl chloride; it is best purified by sublimation, and then crystallises in long, colourless filaments. The anhydride is soluble in chloroform or benzene, and slightly so in ether or light petroleum. T. A. H.

Preparation of *iso*Butyl *p*-Aminobenzoate. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 218389. Compare Abstr., 1909, i, 921).—When *p*-aminobenzoic acid is boiled with *iso*butyl alcohol or iodide, products of therapeutic value as anæsthetics are obtained.

iso*Butyl* p-*aminobenzoate*, colourless needles, m. p. 65°, is prepared by saturating an *iso*butyl-alcoholic solution of the amino-acid with hydrogen chloride at 100°, and isolating the product by the insolubility of its hydrochloride in ether.

iso*Butyl* p-*nitrobenzoate*, yellow needles, m. p. 70°, is similarly prepared from *p*-nitrobenzoic acid; on reduction with aluminium and moist ether, the foregoing compound is obtained. iso*Butyl* p-*β-naphtholazobenzoate*, $C_4H_9\cdot CO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 157—158°, is prepared by the esterification of *p*-*β*-naphtholazobenzoic acid. The solubility of these esters in water is stated in the patent. F. M. G. M.

Alkylation of Aromatic Amino-acids. II. 5-Iodo-2-aminobenzoic Acid and 3 : 5-Di-iodo-2-aminobenzoic Acid. Henry L. Wheeler and Carl O. Johns (*Amer. Chem. J.*, 1910, **43**, 398—411).—When the salts of *o*-, *m*-, and *p*-aminobenzoic acids are treated with alkyl halides, alkylaminobenzoic acids are produced, but esters of the type $NH_2\cdot C_6H_4\cdot CO_2R$ do not seem to be formed. Certain derivatives of the aminobenzoic acids, however, do yield esters of this type, in which the alkyl radicle does not enter the amino-group, and from which the acid can be recovered by hydrolysis. This is the case with the salts of 3 : 5-di-iodo-4-aminobenzoic acid, 3 : 5-dinitro-4-aminobenzoic acid, and 3-nitro-2-aminobenzoic acid, in each of which the substituting atoms or groups are adjacent to the amino-group. 3-Nitro-5-aminobenzoic acid, on the other hand, yields an *N*-alkyl derivative.

It has now been found that 5-iodo-2-aminobenzoic acid gives an *N*-alkyl derivative, whilst 3 : 5-di-iodo-2-aminobenzoic acid yields an ester, the adjacent substituents in this case being CO_2H and I. When potassium 5-iodo-2-aminobenzoate is heated with ethyl iodide, 5-*iodo*-2-*ethylaminobenzoic acid*, m. p. 162° (decomp.), is obtained, which forms minute prisms.

2 : 5-*Di-iodobenzoic acid*, m. p. 183°, obtained by the action of potassium iodide on the product of the diazotisation of 5-iodo-2-aminobenzoic acid, crystallises in slender prisms; its *sodium* salt is described. The *ethyl* ester, m. p. 65°, forms colourless, silky needles.

3 : 5-*Di-iodo*-2-*aminobenzoic acid*, $NH_2\cdot C_6H_2I_2\cdot CO_2H$, m. p. 230—232° (decomp.), obtained by the action of iodine monochloride on a solution

of 5-iodo-2-aminobenzoic acid in dilute hydrochloric acid, crystallises in slender prisms; the *chloride* and the *ammonium* and *sodium* salts have been prepared. The *amide*, m. p. 238—239° (decomp.), forms long needles, and the *ethyl* ester, m. p. 101°, slender prisms. When the product of the diazotisation of this acid is treated with potassium iodide, 2 : 3 : 5-*tri-iodobenzoic acid*, m. p. 224—226°, is produced, which forms colourless, slender prisms; the *sodium* salt is described. 3 : 5-*Di-iodo-2-aminothiolbenzoic acid*, $NH_2 \cdot C_6H_2I_2 \cdot CO \cdot SH$, m. p. 116° (decomp.), obtained by the action of potassium sulphide on 3 : 5-di-iodo-2-aminobenzoyl chloride, forms a red, crystalline powder. When this substance is heated in chloroform solution, it is converted into 3 : 5-*di-iodo-2-aminobenzoyl disulphide*, $(NH_2 \cdot C_6H_2I_2 \cdot CO)_2S_2$, which forms a yellow powder and decomposes at 202°. 3 : 5-*Di-iodo-2-aminobenzanilide*, m. p. 224° (decomp.), obtained by heating the disulphide with aniline, crystallises in slender prisms. E. G.

Preparation of Halogen Derivatives of Phenylglycine-*o*-carboxylic Acid. Badische Anilin- & Soda-Fabrik (D.R.-P. 220839. Compare this vol., i, 318, 319).—The preparation and constitution of nitrogen derivatives of phenylglycine-*o*-carboxylic acids and of anthranilodi-ω-acetic acids have previously been recorded; further work is now described in which halogenated anthranilic acids are employed for the same condensation.

When 4 : 6-dichloroanthranilic acid (m. p. 222—224°) is treated with formaldehyde, a condensation product, needles, m. p. 170°, is obtained, which on subsequent treatment with potassium cyanide yields 3 : 5-*dichloro-ω-cyanomethylanthranilic acid*, colourless needles, m. p. 157—158°, and on subsequent hydrolysis with sodium hydroxide gives 4 : 6-dichlorophenylglycine-2-carboxylic acid, identical with that prepared by chlorinating phenylglycine-*o*-carboxylic acid.

Dibromophenylglycine-o-carboxylic acid, needles, m. p. 245—248°, is prepared in a similar manner from dibromoanthranilic acid (m. p. 225°); the *formaldehyde* product forms needles, m. p. 184—185°; and *dibromo-ω-cyanomethylanthranilic acid* crystallises in prisms, m. p. 185—190°.

Tetrachlorophenylglycine-o-carboxylic acid crystallises from hot water in colourless needles, m. p. 198°; the *formaldehyde* product has m. p. 216°; and *tetrachloro-ω-cyanomethylanthranilic acid* forms minute crystals, m. p. 178°.

The *tetrachloroanthranilic acid* required for the above condensation was obtained from tetrachlorophthalic anhydride by heating with ammonium hydroxide and subsequently treating with sodium hypochlorite; it crystallises from water in slender needles, m. p. 182°; the *calcium* salt forms leaflets; the *barium* salt, needles. F. M. G. M.

New Synthesis of Benzoylenecarbamide. Hermann Finger and W. Zeh (*J. pr. Chem.*, 1910, [ii], 81, 466—470).—*Ethyl cyanoanilide-o-carboxylate*, $CN \cdot NH \cdot C_6H_4 \cdot CO_2Et$, m. p. 176°, obtained by heating ethyl cyanoimidocarbonate and methyl or ethyl anthranilate in the presence of a little cuprous chloride as catalyst, separates from paraldehyde in colourless needles; the *hydrochloride* or the

hydriodide at 200° yields ethyl chloride or iodide and benzoylenecarbamide, which is also produced when the hydrochloride is heated with alcohol or glacial acetic acid, or when the ester itself is heated with hydrochloric or moderately concentrated sulphuric acid.

C. S.

Alkylation of Ethyl Cyanoanilide-*o*-carboxylate. Hermann Finger (*J. pr. Chem.*, 1910, [ii], 81, 470—472).—The treatment of a warm alcoholic solution of ethyl cyanoanilide-*o*-carboxylate (preceding abstract) with sodium ethoxide and methyl sulphate leads to the formation of o-*carbethoxyphenylmethylcarbodi-imide*,

$$NMe{:}C{:}N{\cdot}C_6H_4{\cdot}CO_2Et,$$

m. p. 77·5°, the constitution of which follows from the fact that the *hydrochloride*, $C_{11}H_{12}O_2N_2,HCl$, yields γ-methylbenzoylenecarbamide, m. p. 237·5°, when heated at 100°, or when kept in chloroform for a short time at the ordinary temperature. C. S.

Transformation of Synthetical and Hetero-cinnamic Acids into Storax Acid. Emil Erlenmeyer and G. Hilgendorff (*Ber.*, 1910, 43, 1076—1078. Compare this vol., i, 175; Riiber and Goldschmidt, *ibid.*, 174).—When pure synthetical cinnamic acid or the hetero-acid is boiled with water and animal charcoal, pure storax acid is obtained. There is a loss of some 10% of the original acid, but according to the authors the change cannot be due to the removal of some impurity (substituted cinnamic acids) by the charcoal, as when a mixture of storax acid and a substituted cinnamic acid is boiled with water and charcoal, the substituted acid is not removed. The change is probably due to a molecular rearrangement of some type.

Repeated solution of the hetero-acid in dilute sodium carbonate and precipitation with hydrochloric acid produces a gradual change.

When benzaldehyde and acetic anhydride are heated in a sealed tube at 170° for ten hours and subsequently condensed with sodium acetate, the product is storax-cinnamic acid.

J. J. S.

Phenylglyceric Acid and Phenylpyruvic Acid. Walter Dieckmann (*Ber.*, 1910, 43, 1032—1035).—α-Oxy-βγ-diphenylbutyrolactone (compare this vol., i, 385) is formed when phenylglyceric acid (either isomeride) and benzaldehyde are boiled with glacial acetic and hydrochloric acids. As the lactone is formed by the condensation of benzaldehyde with phenylpyruvic acid, it appeared probable that its formation from phenylglyceric acid was due to the intermediate production of phenylpyruvic acid.

It is now shown that phenylpyruvic acid is formed when the glyceric acid is heated with 20—50% sulphuric acid, or with concentrated hydrochloric acid. The reaction consists in the elimination of water and the molecular rearrangement of the resulting α-hydroxycinnamic acid into phenylpyruvic acid:

$$OH{\cdot}CHPh{\cdot}CH(OH){\cdot}CO_2H \longrightarrow CHPh{:}C(OH){\cdot}CO_2H \longrightarrow CH_2Ph{\cdot}CO{\cdot}CO_2H.$$

When phenylglyceric acid is boiled for some time with acetic anhydride, it yields *α-acetoxycinnamic acid*, $CHPh:C(OAc)\cdot CO_2H$, m. p. 169—171°, which on hydrolysis gives acetic and phenylpyruvic acids. The same acetyl compound is formed when phenylpyruvic acid is boiled with acetic anhydride.

The *diacetyl* derivative of phenylglyceric acid (m. p. 141°) is formed by acetylating the acid with acetic anhydride and a few drops of concentrated sulphuric acid. It crystallises in colourless plates, m. p. 88—90°. J. J. S.

Phenylglycidic Acid. Walter Dieckmann (*Ber.*, 1910, **43**, 1035—1038. Compare Erlenmeyer, Abstr., 1880, 472).—Phenylglycidic acid is not as unstable as stated by Erlenmeyer. It can be obtained by the elimination of halogen hydride from phenyl-α-chloro- or α-bromo-lactic acid, or by the hydrolysis of its ester, and is identical with the compound described by Erdmann (D.R.-P. 107228) as the β-lactone of phenylglyceric acid. Its strongly acidic properties point to the glycide constitution $O<\begin{matrix}CHPh\\ |\\ CH\cdot CO_2H\end{matrix}$ rather than to the lactone formula. It crystallises in colourless plates, m. p. 83—84°, and at the same time evolves carbon dioxide and yields phenylacetaldehyde.

The *normal potassium* salt, $C_9H_7O_3K$, forms anhydrous crystals; the *acid potassium* salt, $KH(C_9H_7O_3)_2,2H_2O$, is very sparingly soluble. J. J. S.

l-Hydroxyphenyl-lactic Acid and its Occurrence in the Urine of Dogs Suffering from Phosphorus Poisoning. Yashiro Kotake (*Zeitsch. physiol. Chem.*, 1910, **65**, 397—401).—*l-Hydroxyphenyl-lactic acid*, $C_9H_{10}O_4,\frac{1}{2}H_2O$, obtained by mixing a solution of tyrosine in sulphuric acid with an aqueous solution of barium nitrite, keeping overnight, filtering, and precipitating with lead acetate, crystallises in long needles, m. p. 162—164° and $[\alpha]_D$ −18°. The *calcium* salt crystallises with $4{\cdot}5H_2O$.

The acid appears to be identical with the product obtained by Blendermann (Abstr., 1883, 876) from the urine of rabbits fed with tyrosine.

The *l*-acid is present in the urine of dogs poisoned with phosphorus. J. J. S.

Synthesis of *p*-Hydroxymandelic Acid and its Occurrence in the Urine in Cases of Acute Yellow Atrophy of the Liver. Alexander Ellinger and Yashiro Kotake (*Zeitsch. physiol. Chem.*, 1910, **65**, 402—413).—*p*-Hydroxymandelic acid has been synthesised from *p*-methoxyacetophenone by the following series of reactions: (1) $OMe\cdot C_6H_4\cdot CO\cdot CH_3 + 3O = OMe\cdot C_6H_4\cdot CO\cdot CO_2H + H_2O$; (2) $OMe\cdot C_6H_4\cdot CO\cdot CO_2H + H_2O = MeOH + OH\cdot C_6H_4\cdot CO\cdot CO_2H$ (compare Bouveault, *Bull. Soc. chim.*, 1897, [iii], 17, 948);

(3) $OH\cdot C_6H_4\cdot CO\cdot CO_2H + 2H = OH\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$,

and the racemic acid has been resolved by means of its cinchonine salt. The active acid thus obtained differs completely from the acid isolated by Schulzen and Riess, in 1869, from the urine of patients

suffering from acute yellow atrophy of the liver, and stated to be *p*-hydroxymandelic acid.

A small amount of a by-product, $C_8H_8O_3$, is obtained in the hydrolysis of *p*-methoxyphenylglyoxylic acid. It is probably a hydroxytoluic acid.

p-*Hydroxymandelic acid*, $OH\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$, crystallises in microscopic plates containing $1H_2O$ and melting at 80—90°. When anhydrous it has m. p. 105—106°.

The *d*-acid crystallises in large plates, contains $1H_2O$, has m. p. 103—104° when anhydrous, and $[\alpha]_D$ +144·4°.

The *cinchonine* salt of the *l*-acid is sparingly soluble, and crystallises in brilliant prisms; the *l*-acid contains $\frac{1}{2}H_2O$. The *calcium* salt, $Ca(C_8H_7O_4)_2,5\frac{1}{2}H_2O$, crystallises in brilliant plates.

Optically active acids could not be detected in the urine of animals to which *p*-hydroxyphenylglyoxylic acid was administered; similar results were obtained when *dl*-hydroxymandelic acid was used.

J. J. S.

Action of Ethyl Diazoacetate on Benzaldehyde. Walter Dieckmann (*Ber.*, 1910, **43**, 1024—1031).—The product obtained by Buchner and Curtius (Abstr., 1885, 1238) by the action of ethyl diazoacetate on benzaldehyde, and regarded as benzylidene*bis*benzoylacetic ester, is shown to be ethyl benzylidenedioxyphenylpropionate, $CHPh<\begin{matrix}O\cdot CHPh\\ |\\ O\cdot CH\cdot CO_2Et\end{matrix}$. The sodium salt, methyl ester, and acid are also the corresponding derivatives of benzylidenedioxyphenylpropionic acid. The m. p. of the acid is 132°, not 130°. When warmed with acetic acid or with aqueous alcohol it is completely hydrolysed to benzaldehyde and phenylglyceric acid (m. p. 121°). When the acid or its ethyl ester is boiled for fifteen hours with an excess of acetic and hydrochloric acids, carbon dioxide is evolved and α-oxy-βγ-diphenylbutyrolactone is formed (Erlenmeyer and Knight, Abstr., 1894, i, 592; Erlenmeyer and Lux, *ibid.*, 1898, i, 668).

In the preparation of the ester from benzaldehyde and ethyl diazoacetate, an *isomeride* of the ester $C_{18}H_{18}O_4$ is obtained. This crystallises in glistening, colourless prisms, m. p. 61—62°, and is much more readily soluble than the ester, m. p. 103—104°, in all solvents. It yields α-oxy-βγ-diphenylbutyrolactone when boiled with glacial acetic and hydrochloric acids.

The corresponding *acid*, $C_{16}H_{14}O_4$, crystallises in microscopic prisms, m. p. 156°, and when its aqueous alcoholic solution is boiled, the acid yields benzaldehyde and phenylglyceric acid (m. p. 141°). The same acid is formed when a mixture of benzaldehyde and phenylglyceric acid is shaken for several hours with five times its weight of 50% sulphuric acid.

The formation of the ester is represented by the following reactions:

$$Ph\cdot CHO + N_2{:}CH\cdot CO_2Et \longrightarrow \begin{matrix}CHPh\text{———}O\\ |\\ CH(CO_2Et)\cdot N\end{matrix}\!\!>\!N ; \begin{matrix}CHPh\text{———}O\\ |\\ CH(CO_2Et)\cdot N\end{matrix}\!\!>\!N +$$

$$Ph\cdot CHO \longrightarrow N_2 + \begin{matrix}CHPh\text{———}O\\ |\\ CH(CO_2Et)\cdot O\end{matrix}\!\!>\!CHPh.$$

J. J. S.

Preparation of Crystalline Salicylosalicylic [*o*-Salicyloxybenzoic] Acids. C. F. Boehringer and Söhne (D.R.-P. 220941. Compare Abstr., 1909, i, 803).—It is found that the ethers of *o*-salicyloxybenzoic acid are readily hydrolysed to the parent acid.

Acetylsalicylosalicylic [2-*o*'-*acetoxybenzoyloxybenzoic*] *acid*,

$$AcO\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

m. p. 159°, is prepared by condensing molecular equivalents of salicylic and *o*-acetoxybenzoic acids with phosphorus trichloride in the presence of dimethylaniline; by treatment with sodium hydroxide at the ordinary temperature, the acetyl group is removed, yielding salicylosalicylic acid.

Ethylcarbonylsalicylosalicylic (2-*o*-*ethylcarbonatobenzoyloxybenzoic*) *acid*, m. p. 122°, obtained by the condensation of molecular proportions of ethylcarbonatobenzoylbenzoic and salicylic acids, undergoes similar hydrolysis on treatment with ammonium hydroxide.

Benzylsalicylosalicylic [2-*o*-*benzyloxybenzoyloxybenzoic*] *acid*,

$$CH_2Ph\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

m. p. 124°, is prepared as follows: *o*-benzyloxybenzoic acid is heated during half an hour with phosphorus trichloride in carbon tetrachloride, extracted with cold sodium hydroxide, the oily portion dried, and the solvent removed by distillation in a vacuum. The residual *o-benzyloxybenzoyl chloride* (a dark oil) is then treated with an equal weight of disodium salicylate and boiled in benzene solution; the mixture is extracted with sodium carbonate, acidified, and again extracted with benzene, when the product is obtained as a syrup which subsequently solidifies. F. M. G. M.

Preparation of Salicylic Esters of Dihydroxyalkylaliphatic Acid Esters. Les Etablissements Poulenc Frères and Ernest Fourneau (D.R.-P. 221262).—When the esters of halogenalkylhydroxy-aliphatic acids of the general formula:

$$CH_2X\cdot CR(OH)\cdot CO_2R'$$

(X = halogen, R and R' = alkyl) are heated with salicylic acid or its salts, compounds of the type $OH\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CR(OH)\cdot CO_2R$ and of great therapeutic value are obtained.

Ethyl β-salicyloxy-α-hydroxyisobutyrate,

$$OH\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CMe(OH)\cdot CO_2Et,$$

m. p. 51—52°, is prepared by heating sodium salicylate with ethyl β-chloro-α-hydroxy*iso*butyrate at 180—185°; it is insoluble in water, but dissolves in sodium hydroxide, by which it is slowly decomposed.

Propyl β-salicyloxy-α-hydroxyisobutyrate,

$$OH\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CMe(OH)\cdot CO_2\cdot C_3H_7,$$

is analogously prepared, but in this case it is advisable to employ some reduced copper and potassium iodide as catalysts and heat at a temperature of 260—280°; it is an odourless syrup, b. p. 203°/15 mm., very sparingly soluble in water.

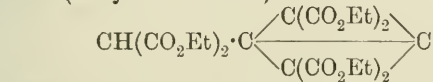
The iso*amyl* ester, b. p. 200°/11 mm., has a powerful odour, and is insoluble in water. F. M. G. M.

New Cyclic Compounds from Ethyl Dicarboxyglutaconate. Max Guthzeit and Erich Hartmann (*J. pr. Chem.*, 1910, [ii], 81, 329—381).—*Ethyl α-chlorodicarboxyglutaconate*,

$$C(CO_2Et)_2{:}CH\cdot CCl(CO_2Et)_2,$$

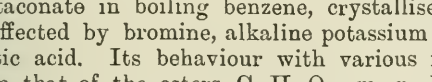
obtained by the action at the ordinary temperature of chlorine on ethyl dicarboxyglutaconate or on a chloroform solution of ethyl sodiodicarboxyglutaconate (Coutelle, Abstr., 1906, i, 139), is a colourless, odourless, mobile liquid, which does not give a coloration with ferric chloride, and is reduced by zinc and acetic acid to *ethyl dicarboxyglutarate*, b. p. 192°/12 mm. *Ethyl αβ-dibromodicarboxyglutarate*, obtained by the action at 0° of bromine in chloroform solution of the ester in intense sunlight, is a viscous liquid, which cannot be distilled and slowly evolves hydrogen bromide, forming *ethyl α-bromodicarboxyglutaconate*, which can also be prepared in a similar manner to the corresponding chloro-compound.

The first step in a series of reactions suggested for the synthesis of ethyl *cyclo*hexane-1 : 1 : 2 : 2 : 4 : 4 : 5 : 5-octacarboxylate is the action of iodine on ethyl sodiodicarboxyglutaconate. The reaction, however, does not follow the expected course: $2CNa(CO_2Et)_2\cdot CH{:}C(CO_2Et)_2 + I_2 = 2NaI + C(CO_2Et)_2{:}CH\cdot C(CO_2Et)_2\cdot C(CO_2Et)_2\cdot CH{:}C(CO_2Et)_2$, but results in the formation of a saturated *ester*, $C_{30}H_{42}O_{16}$, m. p. 86°, which, in consequence of the transformations described below, is regarded as ethyl 2 : 2 : 4 : 4-tetracarboxy*dicyclo*-0 1 1-butane-1 : 3-dimalonate (Baeyer's notation):



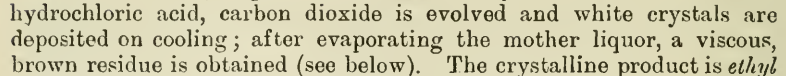
The ester is obtained in more than 90% yield by carefully observing the following conditions. Finely powdered ethyl sodiodicarboxyglutaconate is added to a cold solution of iodine in toluene. The mixture is stirred as rapidly as possible (3000 revolutions per minute), and is then heated. The viscous liquid obtained after the removal of the toluene is mixed with a little ether, and placed in a desiccator which is rendered vacuous; after half an hour the yellow solid is collected, and recrystallised from ether by the addition of petroleum. The ester, which can also be obtained by the interaction of (i) ethyl sodiodicarboxyglutaconate and ethyl α-bromodicarboxyglutaconate in boiling xylene, (ii) the sodio-compound and ethyl α-chlorodicarboxyglutaconate in xylene at 180°, (iii) sulphur and ethyl cupridicarboxyglutaconate in boiling benzene, crystallises in stout prisms, and is unaffected by bromine, alkaline potassium permanganate, or zinc and acetic acid. Its behaviour with various reagents is quite different from that of the esters, $C_{30}H_{44}O_{16}$, m. p. 103° and 88° respectively, obtained by Guthzeit, Weiss, and Schäfer (Abstr., 1909, i, 933), which are derivatives of *cyclo*butane.

When an ethereal solution of the ester, m. p. 86°, is treated with alcoholic sodium ethoxide, and after ten minutes the mixture is added to petroleum, a tetra-sodium *derivative*, $C_{26}H_{30}O_{16}Na_4$, is precipitated as a red, amorphous powder. The acidification of an alcoholic solution of this sodium derivative yields a *hexa-ester dicarboxylic acid*,



m. p. 193°, which forms a white, crystalline *barium* salt and a light green, amorphous *copper* salt, $C_{26}H_{32}O_{16}Cu$, and regenerates the original ester, m. p. 86°, on treatment with alcoholic hydrogen chloride.

When the ester, m. p. 86°, is heated for fifty hours with concentrated hydrochloric acid, carbon dioxide is evolved and white crystals are deposited on cooling; after evaporating the mother liquor, a viscous, brown residue is obtained (see below). The crystalline product is *ethyl* 2 : 2 : 4 : 4-*tetracarboxy*dicyclo-0 1 1-*butane*-1 : 3-*diacetic acid*,

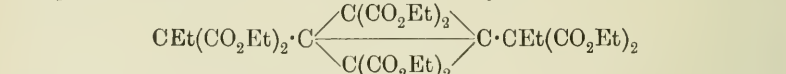


m. p. 152°, which crystallises with $3H_2O$, forms a *zinc* salt,

$$C_{20}H_{24}O_{12}Zn,$$

and a *silver* salt, $C_{20}H_{24}O_{12}Ag_2$, is also obtained by heating the hexa-ester dicarboxylic acid, m. p. 193°, with concentrated hydrochloric acid and yields by esterification with alcoholic hydrogen chloride the corresponding *hexa*-ester, m. p. 71°, which is characterised by its pronounced property of crystallising. 2 : 4-*Dicarboxy*dicyclo-0 1 1-*butane*-1 : 3-*diacetic acid*, $CO_2H\cdot CH_2\cdot C(CH(CO_2H))_2\cdot C\cdot CH_2\cdot CO_2H$, is a hygroscopic, amorphous powder, which is obtained by hydrolysing the ester, m. p. 86°, the hexa-ester dicarboxylic acid, m. p. 193°, or the tetra-ester dicarboxylic acid, m. p. 152°, with 10% aqueous-alcoholic potassium hydroxide, or by the prolonged heating of the previously-mentioned viscous, brown residue with concentrated hydrochloric acid; the *methyl* and the *ethyl* esters, prepared from the silver salt, are viscous liquids, which instantly decolorise potassium permanganate.

The presence of two malonate groups in the ester, m. p. 86°, cannot be proved satisfactorily by alkylation, since the sodio-derivative cannot be obtained unhydrolysed, and the action of dry, amalgamated, granulated zinc and ethyl iodide on the ester results in the formation of an inseparable mixture of the di- and tetra-ethylated derivatives,



and $CO_2Et\cdot CEt_2\cdot C(C(CO_2Et)_2)_2\cdot C\cdot CEt_2\cdot CO_2Et$. The object in view can be attained by bromination, since the ester, m. p. 86°, in boiling carbon tetrachloride is converted by bromine in sunlight into the dibromo-*compound*, $CBr(CO_2Et)_2\cdot C(C(CO_2Et)_2)_2\cdot C\cdot CBr(CO_2Et)_2$, from which the ester, m. p. 86°, is regenerated by zinc and acetic acid. The bromination of the ester, m. p. 86°, in boiling acetic acid in direct sunlight yields a tetrabromo-*compound*, which must have the constitution $CO_2Et\cdot CBr_2\cdot C(C(CO_2Et)_2)_2\cdot C\cdot CBr_2\cdot CO_2Et$, since it is reduced by zinc and acetic acid to the hexa-ester, m. p. 71°. The chlorination of the ester, m. p. 86°, in boiling carbon tetrachloride in sunlight yields a viscous tetrachloro-*compound*, $C_{24}H_{30}O_{12}Cl_4$, the constitution of which is indicated by its reduction to the hexa-ester,

m. p. 71°. When the chlorination, however, is effected in the dark, an isomeric tetrachloro-*compound* is obtained, to which the constitution $CCl(CO_2Et)_2\cdot C\begin{<}\begin{matrix}CCl(CO_2Et)\\ \\ CCl(CO_2Et)\end{matrix}\end{>}C\cdot CCl(CO_2Et)_2$ is ascribed. It is reduced by zinc and acetic acid to *ethyl* 2 : 4-*dicarboxy*dicyclo-011-*butane*-1 : 3-*dimalonate*, $CH(CO_2Et)_2\cdot C\begin{<}\begin{matrix}CH(CO_2Et)\\ \\ CH(CO_2Et)\end{matrix}\end{>}C\cdot CH(CO_2Et)_2$, a mobile liquid which instantly decolorises potassium permanganate, yields an amorphous tetracarboxylic *acid*, $C_{10}H_{10}O_8$, by hydrolysis with concentrated hydrochloric acid, and forms a yellow tetrasodio-*derivative*, $C_{20}H_{22}O_{12}Na_4$, the acidification of the alcoholic solution of which yields a liquid *tetra-ester dicarboxylic acid*,

$$CO_2Et\cdot CH(CO_2H)\cdot C\begin{<}\begin{matrix}CH(CO_2Et)\\ \\ CH(CO_2Et)\end{matrix}\end{>}C\cdot CH(CO_2H)\cdot CO_2Et,$$

which instantly decolorises potassium permanganate. C. S.

Simple Method for the Preparation of Large Quantities of Ellagic Acid. Hans Trunkel (*Arch. Pharm.*, 1910, **248**, 202—204).—A 1% solution of tannin is treated with sufficient 5% sodium carbonate to adjust the proportion of tannin to carbonate to 2 : 1 ; the mixture is exposed to the air for eight days in flat vessels with occasional stirring. The resulting sodium ellagate, after decantation of the liquor, is treated with alcohol to facilitate filtration, and is obtained in 47% yield. The acid is liberated by cold dilute hydrochloric acid, washed with alcohol, and crystallised from pyridine ; yield 50%. C. S.

Tannins. III. Ellagitannic Acid. Maximillian Nierenstein (*Ber.*, 1910, **43**, 1267—1270. Compare Abstr., 1909, i, 174, and Perkin and Nierenstein, Trans., 1905, **87**, 1412).—Pure ellagitannic acid has been prepared by repeatedly treating the acid from myrobalan with alkali and ethyl chloroformate, and then decomposing with pyridine according to Fischer's method. The acid has the composition $C_{26}H_{28}O_{19},3H_2O$, crystallises from a mixture of pyridine and glacial acetic acid in pale yellow plates, m. p. 329—336°, after sintering at 300—306°, and $[\alpha]_D^{17}$ +18·02°.

When boiled with dilute sulphuric acid, it yield ellagic acid, but is not decomposed when boiled with 10% sodium carbonate solution. The acid is hydrolysed by emulsin to luteo-acid, and is thus a a glucoside of luteo-acid (*loc. cit.*), and one of the dextrose molecules is probably attached to the position 6. J. J. S.

Action of Light on Benzaldehyde in Presence of Iodine. Luigi Mascarelli (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 383—389). —The action of light on benzaldehyde in presence of iodine or iodoxybenzene or iodosobenzene yields (1) benzoic acid ; (2) a *dimeric benzaldehyde*, which is a dense colourless liquid, b. p. 189—191°/18 mm. ; (3) the trimeric and (4) tetrameric benzaldehydes previously

described (compare Mascarelli, Abstr., 1906, i, 962; Ciamician and Silber, Abstr., 1909, i, 306); (5) traces of hydrobenzoin; (6) stilbene, and (7) an oil, not yet characterised. The relative proportions of these products vary with the compound mixed with the aldehyde, the best yield of the oil being obtained when iodine is employed. The fact that the dimeride is not obtained by the action of light on the aldehyde alone (compare Ciamician and Silber, *loc. cit.*) indicates that its formation is due to the presence of traces of iodine liberated from iodobenzene, into which both iodoxy- and iodoso-benzene tend to become transformed: $C_6H_5IO_2 \longrightarrow C_6H_5IO \longrightarrow C_6H_5I$. T. H. P.

Preparation of Salts of *m*-Aminobenzaldehyde in the Presence of Anhydro-*o*-aminobenzaldehyde. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 218364).—The product obtained by reducing the crude mixture of nitrobenzaldehydes with sodium hyposulphite contains about 25% of *o*-aminobenzaldehyde; the separation of this from the meta-isomeride can be effected by treatment with an adequate quantity of hydrochloric acid, when *o*-aminobenzaldehyde is completely precipitated in the form of its anhydride,

$$NH_2 \cdot C_6H_4 \cdot CH{:}N \cdot C_6H_4 \cdot CHO,$$

the *m*-aminobenzaldehyde remaining in solution in the form of its hydrochloride to be subsequently separated by known methods. The *o*-anhydride by further treatment with acids is readily resolved into pure *o*-aminobenzaldeyhyde; the hydrochloric acid may be replaced by oxalic or sulphuric acid in this reaction. F. M. G. M.

Preparation of Nitrobenzaldehyde Sulphides. Georg Kränzlein (D.R.-P. 219839).—Chloronitrobenzaldehydes, which contain the chlorine atom in an *o*- or *p*-position to the nitro-group, react readily with sodium thiosulphate, yielding nitrobenzaldehyde sulphides.

Nitrobenzaldehyde sulphide [*2-nitro-4-aldehydophenyl sulphide*], $C_{14}H_8O_6N_2S$, m. p. 194·5—195°, is prepared by warming 4-chloro-3-nitrobenzaldehyde dissolved in alcohol with aqueous sodium thiosulphate at 70°, when the product rapidly separates in yellow crystals; the isomeric 4-nitro-2-aldehydophenyl sulphide obtained from 2-chloro-5-nitrobenzaldehyde has m. p. 297—297·5°. F. M. G. M.

Decomposition of Piperonal on Heating with Dilute Hydrochloric Acid. W. Schut (*Chem. Weekblad*, 1910, 7, 371—374. Compare Fittig and Remsen, this Journ., 1873, 1143).—The black powder obtained by Fittig and Remsen by the action of dilute hydrochloric acid on piperonal contains only 67·3% of carbon. The author attributes its formation to condensation resulting from the aldehydic nature of piperonal. He does not consider that formaldehyde is produced by the action of water, and then decomposed into carbon and water. A. J. W.

Action of Carbon Disulphide and Potassium Hydroxide on Acetophenone. C. Kelber (*Ber.*, 1910, 43, 1252—1259).—By the interaction of acetophenone, carbon disulphide, and potassium hydroxide

at the temperature of the water-bath, a *substance*, $C_9H_8OS_2$, is formed of faintly acid nature crystallising in lustrous, golden-yellow plates, m. p. 63—64°. The *dimethyl ether* forms bright yellow needles, m. p. 93—94°; the *dibenzyl ether* crystallises in thin, yellow, glistening needles, m. p. 113°, whereas the *monobenzyl ether* forms yellow crystals, m. p. 49—50°. The *dibenzoyl* derivative forms short, yellow, refractive crystals, m. p. 113—114°. The substance forms soluble, orange-red salts with alkali hydroxides, and insoluble coloured salts with the heavy metals.

Concentrated potassium hydroxide decomposes it into benzoic acid and hydrogen sulphide, alcoholic ammonia forms ammonium thiocyanate and acetophenone, and boiling aniline gives rise to benzanilide. Aniline in the cold forms a *compound*, $C_{15}H_{13}ONS$, crystallising in aggregates of light yellow needles, m. p. 78·5°, of which the *phenacyl* derivative, $C_{15}H_{12}ONS{\cdot}CH_2{\cdot}COPh$, crystallises in bunches of faintly green needles, m. p. 160—161°. On oxidation, phenylcarbylamine, benzoic and sulphuric acids are obtained.

The constitution $C_6H_5{\cdot}CO{\cdot}CH{:}C(SH)_2$ is ascribed to the compound $C_9H_8OS_2$, although the keto-group cannot be identified by hydroxylamine or phenylhydrazine. By the action of bromine on the dimethyl-derivative, a labile red *additive* product, $COPh{\cdot}CHBr{\cdot}CBr(SMe)_2$, is first formed, from which hydrogen bromide is eliminated with formation of the stable *monobromo*-derivative, $COPh{\cdot}CBr{:}C(SMe)_2$, crystallising in lustrous, light yellow crystals, m. p. 52·5—53·5°.

Oxidation with ammonium persulphate in alkaline solution yields a *compound*, $C_{18}H_{12}O_2S_3$, crystallising in golden-yellow needles, m. p. 206—207°. E. F. A.

"Dimorphism" of Benzophenone. Karl Schaum (*Chem. Zeit.*, 1910, **34**, 417).—The two modifications of benzophenone in the fused state exhibit small but definite differences in their physical properties (refraction and viscosity). It is probable that the molecules of the stable α-modification change when the substance is fused into those of the β-form, the concentration of which increases with the degree and the duration of the heating. The labile crystalline modification contains varying quantities of the α- and the β-forms; when the labile form changes to the stable, all the β-molecules have been converted into α-molecules. C. S.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. XIII. Derivatives of *cyclo*Hexane. Elmer P. Kohler and M. Cloyd Burnley (*Amer. Chem. J.*, 1910, **43**, 412—418).—Earlier work has shown that many unsaturated ketones unite with organic magnesium compounds to form both $\alpha\beta$- and $\alpha\delta$-additive products, in proportions depending on the nature of the magnesium compound as well as on that of the ketone. The mode of addition to substances containing the chain C:C·C:O is affected more by the number and arrangement of the hydrocarbon residues in the ketone than by their chemical character. The relation between the mode of addition and the nature of the magnesium compound is less easily determined, but the results obtained by the action of various magnesium compounds on styryl ethyl ketone (Abstr., 1907, i, 1052)

suggest that the mode of addition to any given ketone depends more on the chemical than the spatial character of the hydrocarbon residues contained in the magnesium compound.

The experiments now described support these conclusions. Magnesium *cyclo*hexyl bromide can be obtained in a yield of more than 95% by a modification of Freundler and Damond's method (Abstr., 1905, i, 890). It reacts with styryl methyl ketone to form *α-phenyl-α-cyclohexylbutan-γ-one*, $C_6H_{11}\cdot CHPh\cdot CH_2\cdot COMe$, m. p. 67°, which crystallises in colourless needles; a yield of 37·2 grams was obtained from 36·4 grams of the ketone. From 42 grams of anisylideneacetone, 44 grams of *α-anisyl-α-cyclohexylbutan-γ-one*,

$$C_6H_{11}\cdot CH(C_6H_4\cdot OMe)\cdot CH_2\cdot COMe,$$

b. p. 218°/18 mm., were obtained as a viscous liquid. *α-Phenyl-α-cyclohexylpentan-γ-one*, $C_6H_{11}\cdot CHPh\cdot CH_2\cdot COEt$, m. p. 71°, obtained in a yield of 43 grams from 40 grams of styryl ethyl ketone, forms colourless needles. *Phenylcyclohexylpropiophenone*, $C_6H_{11}\cdot CHPh\cdot CH_2\cdot COPh$, m. p. 122—122·5°, obtained from phenyl styryl ketone in a yield of nearly 95%, crystallises in needles.

Styryl cyclo*hexyl ketone*, $CHPh:CH\cdot CO\cdot C_6H_{11}$, m. p. 58°, prepared by condensing methyl *cyclo*hexyl ketone with benzaldehyde, crystallises in colourless plates and unites with bromine to form a *dibromide*, m. p. 139°. This ketone reacts with magnesium ethyl bromide with production of *phenylbutyl* cyclo*hexyl ketone*, $CHPhEt\cdot CH_2\cdot CO\cdot C_6H_{11}$, b. p. 188°/16 mm. *Diphenylethyl* cyclo*hexyl ketone*,

$$CHPh_2\cdot CH_2\cdot CO\cdot C_6H_{11},$$

b. p. 250°/17 mm., m. p. 68°, obtained by the action of magnesium phenyl bromide on styryl *cyclo*hexyl ketone, forms long, colourless needles. E. G.

Preparation of Hydrocarbons, Acids, Amides, and Thiophens by the Action of Ammonium Sulphide on Fatty Aromatic Ketones. Conrad Willgerodt and Theodor Scholtz (*J. pr. Chem.*, 1910, [ii], **81**, 382—402).—The work is an extension of that previously recorded (Abstr., 1909, i, 716; this vol., i, 117). A copper autoclave lined with lead is used. Experiments on *p*-tolyl methyl ketone, *p*-xylyl methyl ketone, mesityl methyl ketone, α-naphthyl methyl ketone, phenyl ethyl ketone, and colourless solid ammonium sulphide at about 215° show that (1) reduction of ketones containing methyl and ethyl radicles to the corresponding hydrocarbons occurs; (2) the acid amide and, in much smaller amount, the acid are always formed; (3) thiophen derivatives are obtained only in the cases of phenyl methyl ketone and *p*-tolyl methyl ketone; (4) the presence of complex aliphatic and aromatic radicles in the ketone hinders the formation of thiophens.

Also, the following ketones have been heated with solid ammonium sulphide: ψ-Cumyl methyl ketone yields 1 : 2 : 4-trimethyl-5-ethylbenzene, 15% of ψ-cumylacetamide, and 7% of the acid; ψ-cumyl ethyl ketone yields 1 : 2 : 4-trimethyl-5-propylbenzene, 6% of *β-ψ-cumylpropionamide*, $C_6H_2Me_3\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, m. p. 157°, and only a trace of the *acid*, m. p. 92°; ψ-cumyl propyl ketone yields 6% of *γ-ψ-cumylbutyramide*, m. p. 153°, and a trace of the *acid*, m. p. 71°; ψ-cumyl

*iso*propyl ketone yields 0·5% of *ψ-cumyl*iso*butyramide*, m. p. 158°. *ψ-Cumyl*iso*butyl ketone*, b. p. 282°, obtained from *iso*valeryl chloride and *ψ*-cumene by the Friedel-Craft reaction (*phenylhydrazone* consists of white prisms which decompose by heating), yields practically no amide when heated with ammonium sulphide at 180°. With the last ketone, therefore, the Willgerodt reaction reaches its limit in this series of ketones (compare Willgerodt and Merk, Willgerodt and Hambrecht, *loc. cit.*).

The following ketones react with solid ammonium sulphide at 215°. *m*-Diphenylyl methyl ketone yields 20% of m-*diphenylylacetamide*, $C_6H_4Ph\cdot CH_2\cdot CO\cdot NH_2$, which decomposes without melting, and only a trace of the *acid*, m. p. 146°. m-*Diphenylyl ethyl ketone*, $C_6H_4Ph\cdot COEt$, m. p. 89°, b. p. 344°, obtained from equal molecular quantities of diphenyl and propionyl chloride by the Friedel-Craft reaction, forms an *oxime*, m. p. 159°, and a *phenylhydrazone*, m. p. 122°, and by heating with ammonium sulphide yields 6% of *β*-m-*diphenylylpropionamide*, $C_6H_4Ph\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, m. p. 196°, and hardly a trace of the *acid*, m. p. 145°. m-*Diphenylyl propyl ketone*, m. p. 74°, b. p. 354—355°, prepared from diphenyl and butyryl chloride, forms an *oxime*, m. p. 100°, and *phenylhydrazone*, m. p. 94°, and gives a very small yield of *γ*-m-*diphenylylbutyramide*, m. p. 144° (the *acid* has m. p. 100°), with ammonium sulphide. m-*Diphenylyl* iso*propyl ketone*, m. p. 56°, b. p. 346—347°, forms an *oxime*, m. p. 54°, and *phenylhydrazone*, m. p. 99°, and does not yield an amide or acid with ammonium sulphide. m-*Diphenylyl* iso*butyl ketone*, m. p. 63°, b. p. 356° (*oxime*, m. p. 131°; *phenylhydrazone*, m. p. 102·5°), does not yield an amide or acid with ammonium sulphide at 190°. C. S.

Trialkylacetonaphthones and their Decomposition by Sodamide. V. Volmar (*Compt. rend.*, 1910, **150**, 1174—1177. Compare Haller and Bauer, Abstr., 1909, i, 108—131).—The ultimate product obtained when *α*-naphthyl methyl ketone is methylated with sodamide and methyl iodide is *α-naphthyl* tert.-*butyl ketone*, $C_{10}H_7\cdot CO\cdot CMe_3$, m. p. 73—74°, b. p. 183—186°/19 mm.; this compound does not form a picrate, but yields with difficulty an *oxime*, m. p. 198—199°. *β-Naphthyl* tert.-*butyl ketone*, obtained in the same way, is a faintly coloured, oily liquid, b. p. 184—186°/16 mm.; the *picrate* crystallises in yellow needles, m. p. 74—75°, whilst the *oxime*, prepared by Crismer's method, has m. p. 193—194°. *α-Naphthyl* tert.-*amyl ketone*, $C_{10}H_7\cdot CO\cdot CMe_2Et$, is a pale yellow oil, b. p. 185—187°/14 mm., forming an *oxime*, m. p. 171—172°; the corresponding *β*-compound has b. p. 187—189°/14 mm., and forms an *oxime*, m. p. 183—184°.

On treating the foregoing ketones with sodamide, the usual decomposition takes place, fission occurring as in the case of the phenyl naphthyl ketones studied by Lucas (Abstr., 1909, i, 488).

W. O. W.

Derivatives of Resorcinol. Hugo Kauffmann and Paul Pannwitz (*Ber.*, 1910, **43**, 1205—1213. Compare Abstr., 1905, i, 280, 773; 1909, i, 99).—2 : 4-Dimethoxybenzophenone, prepared by the interaction of resorcinol dimethyl ether and benzoyl chloride in

presence of aluminium chloride, is a colourless compound, m. p. 83° (compare König and von Kostanecki, 1907, i, 62). It gives a yellow coloration with concentrated sulphuric acid. The *phenylhydrazone* crystallises in yellow needles, m. p. 146°; the *oxime* was obtained in two modifications, m. p. 175° and 162°, the less fusible compound being less acid and more soluble in alcohol. A by-product of the above reaction is 2-hydroxy-4-methoxybenzophenone, crystallising in long, slender, yellow needles, m. p. 62° (compare König and Kostanecki, *loc. cit.*).

Nitro-2 : 4-dimethoxybenzophenone was obtained in almost colourless plates, m. p. 153°.

By the action of phosphorus pentachloride, dimethoxybenzophenone is converted quantitatively into the *monochloro*-derivative, which is also formed by the action of chlorine on a solution of the ketone in acetic acid; it forms colourless crystals, m. p. 144°.

Dimethoxybenzophenone in ethereal solution reacts with bromobenzene and magnesium, forming 2 : 4-*dimethoxytriphenylcarbinol*, which crystallises in colourless plates, m. p. 138°, and gives a dark red coloration with concentrated sulphuric acid. It is very readily reduced by zinc dust and acetic acid to 2 : 4-dimethoxytriphenylmethane, crystallising in colourless plates, m. p. 124°. It dissolves in concentrated sulphuric acid with a yellow coloration, and is converted by phosphorus pentachloride into a monochloro-derivative.

Aluminium chloride converts dimethoxytriphenylcarbinol into 3-*hydroxy*-9-*phenylxanthen*, $OH\cdot C_6H_3<\begin{matrix}CHPh\\ \\ O\end{matrix}>C_6H_4$; this crystallises in colourless, matted needles, m. p. 196°. It is soluble in alkali, and contains only one hydroxyl group, as it forms an *acetate*, crystallising in colourless rods, m. p. 158°, and a *benzoate*, separating in long, thin prisms, m. p. 194°. All three substances are characterised by a very intense green fluorescence in concentrated sulphuric acid.

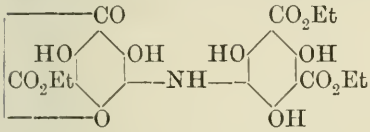
E. F. A.

Formation of Keto-asarone. Vincenzo Paolini (*Gazzetta*, 1910, 40, i, 113—116).—It has been shown by Wallach and Pond (Abstr., 1896, i, 94) and by Hell and Portmann (Abstr., 1896, i, 357) that the action of alcoholic potassium hydroxide on dibromides of compounds containing a propenyl chain gives rise to ketones of the general formula R·COEt. Previous attempts to isolate in this way the ketone corresponding with dibromoasarone (compare Beckstroem, Abstr., 1904, i, 409; Széki, Abstr., 1906, i, 660) have been unsuccessful.

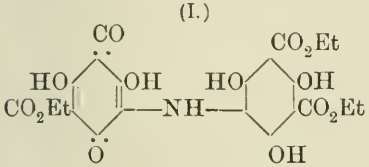
The author finds that the conditions employed by Beckstroem lead to the formation of an oil, which, when freed from bromine by the action of zinc dust and aqueous potassium hydroxide and purified by boiling with 20% sulphuric acid solution, consists of the pure *ketone*, $C_{12}H_{16}O_4$, which forms shining, white needles, softening at 106°, m. p. 108°, b. p. 186°/13 mm. This ketone is the α-ketone, R·COEt, since it yields propionic acid when heated in a sealed tube with sulphuric acid. The *semicarbazone*, $C_{13}H_{19}O_4N_3$, forms shining, white plates, m. p. 182—183°.

T. H. P.

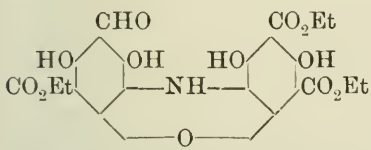
Formation of a Keten-like Quinone and Other Completely Substituted Derivatives of Diphenylamine. Exchange of Alkyl in Esters by means of Alcoholic Ammonium Hydroxide. Hermann Leuchs and George Theodorescu (*Ber.*, 1910, 43, 1239—1251. Compare Abstr., 1909, i, 106).—By the action of cold concentrated nitric acid on ethyl phloroglucinoldicarboxylate (Abstr., 1909, i, 106), three complicated substances were obtained, two being isomerides of the formula $C_{22}H_{21}O_{13}N$, and the third having the composition $C_{22}H_{21}O_{12}N$. It is now shown that ethyl hexahydroxydiphenylaminetetracarboxylate, prepared by condensation of ethyl aminophloroglucinoldicarboxylate in cold alcoholic solution, is the parent substance of these compounds. Cold nitric acid converts it into a mixture in equal parts of the lactonic ester, $C_{22}H_{21}O_{13}N$, and the ester, $C_{22}H_{21}O_{12}N$ (*loc. cit.*, p. 107). The ester, $C_{24}H_{27}O_{14}N$, is consequently regarded as an intermediate stage in the action of nitric acid on ethyl phloroglucinoldicarboxylate; alcohol is subsequently eliminated from it in one of two ways. Formula I represents the yellow ester, $C_{22}H_{21}O_{13}N$; formula II corresponds with the isomeric dark red ester, which contains the group $>C{:}CO$, characteristic of the ketens. This may be reduced by sulphurous acid or by boiling with alcohol, two atoms of hydrogen being added and water eliminated, forming an hydroxyaldehyde with a *p*-oxazine ring (annexed formula). Reduction with zinc dust and acetic acid converts this aldehyde into the corresponding alcohol.



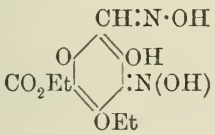
(I.)



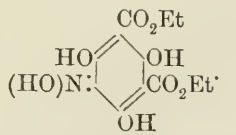
(II.)



By the action of hydroxylamine, the oxazine ring is broken, the nitrogen eliminated as ammonia, and the two products obtained have the formulæ:



and



Diethyl tetrahydroxybenzenedicarboxylate, prepared by boiling the hydrochloride of ethylaminophloroglucinoldicarboxylate with water, forms long, colourless needles, m. p. 116—117°, and dissolves in sodium carbonate with a red, in ammonia with a reddish-yellow, coloration.

Ethyl hexahydroxydiphenylaminetetracarboxylate, $C_{24}H_{27}O_{14}N$, was obtained in colourless, glistening, obliquely-cut prisms or four-sided plates, m. p. 189—190° (corr.). The *acetyl* derivative crystallises from alcohol in heavy, four-sided plates, m. p. 211—212° (corr.). A by-

product of the condensation is a substance, $(C_{22}H_{21}O_{13}N)_x$, separating in intensely yellow-coloured needles, m. p. 265° (decomp.), which is regarded as a polymeride of the lactonic ester.

Reduction of the aldehyde ester, $C_{22}H_{21}O_{12}N$, converts it into the corresponding *alcohol*, $C_{22}H_{23}O_{12}N$, which crystallises in golden-yellow needles, m. p. 188—190° (corr.). Decomposition of this aldehyde with hydroxylamine yields an *oxime*, $C_{12}H_{14}O_7N_2$, crystallising in pointed, dark red prisms, m. p. 137—138°, together with an *oxime*, $C_{12}H_{13}O_8N$, which separates in yellow needles, m. p. 140—141°. The latter compound is also obtained by the action of hydroxylamine on ethyl tetrahydroxybenzenedicarboxylate.

The *hydrochloride* of *aminophloroglucinol*, $C_6H_2(OH)_3{\cdot}NH_2$, prepared by reduction of nitrophloroglucinol with zinc and hydrochloric acid, was obtained in large, colourless plates (decomp. 230°). Condensation of this in alcoholic solution gave a dark violet substance insoluble in all reagents.

A weak solution of ammonia in methyl alcohol converts diethylphloroglucinoldicarboxylate into the corresponding methyl ether, which conversely is converted by ammonia in ethyl alcohol into the ethyl ester. The *dimethyl* ester forms colourless needles, m. p. 145—146°. The ethyl ester is not converted by prolonged boiling with methyl alcohol.

The *methyl* ester *amide* of phloroglucinoldicarboxylate separates in lancet-shaped crystals, m. p. 240° (decomp.).

Similarly, diethyl malonate, when left in contact with methyl-alcoholic ammonia for some days at 10°, is converted into dimethyl malonate.

E. F. A.

Preparation of Halogen Anthraquinonesulphonic Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 217552).—When α- or β-chloroanthraquinone is treated with fuming sulphuric acid (40% anhydride) or with chlorosulphonic acid at 180°, a mixture of two sulphonic acids is obtained; these can be separated by fractional crystallisation, or by subsequent fusion with potassium hydroxide, yielding a mixture of anthrapurpurin and flavopurpurin. 1 : 8-Dichloroanthraquinone under similar conditions forms 1 : 8-dichloroanthraquinone sulphonic acid.

F. M. G. M.

[Preparation of Anthraquinone Derivatives.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 220581).—A tabulated list of compounds prepared by the condensation of 4-amino-1-benzoylaminoanthraquinone with numerous halogenated aminoanthraquinones in boiling nitrobenzene solution in the presence of cupric chloride and sodium acetate. The colours of the solutions in concentrated sulphuric acid, pyridine, and when dyed on wool are described in the original.

F. M. G. M.

Preparation of Nitrogen Derivatives of Anthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 218571).—When aminoanthraquinones and epichlorohydrin are boiled together in acetic acid solution, condensation takes place, yielding compounds of value in the colour industry; the products thus obtained from α-amino-

anthraquinone, 1 : 5-diaminoanthraquinone, 1 : 4-aminohydroxyanthraquinone, and *p*-diaminoanthrarufindisulphonic acid are mentioned, and the colour of their solution in various solvents tabulated.

F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. Badische Anilin- & Soda-Fabrik (D.R.-P. 220579).—The condensation of aminoanthraquinones with halogen ketones of the general formula H·R·CO·R·H, where R is a substituted or unsubstituted aromatic or aliphatic residue, and H a halogen, yields products of the type : A·NH·R·CO·R·NH·A ; A = anthraquinone residue.

The patent contains particulars of the condensation of 1-aminoanthraquinone with 4 : 4′-dichlorobenzophenone and with α : 4-dichloroacetophenone in the presence of cuprous chloride and sodium acetate in boiling nitrobenzene solution. The colours of these substances in various strengths of sulphuric acid solution are tabulated.

F. M. G. M.

Retene. A. Heiduschka and E. Scheller (*Arch. Pharm.*, 1910, 248, 89—101).—Tetrabromoretene can be obtained in good yield by adding bromine to retene, heating the mixture on the water-bath until the evolution of hydrogen bromide and bromine ceases, washing the mixture with boiling alcohol, and crystallising the residue from carbon disulphide. By treating its solution in boiling acetic acid with a hot mixture of chromic and acetic acids, *tribromoretenequinone*, $C_{18}H_{13}Br_3O_2$, m. p. 180°, is obtained, and also when the oxidation is effected by boiling acetic and fuming nitric acids. In its behaviour the quinone is quite analogous to retenequinone, yielding *tribromoresazine*,

$$C_{16}H_{13}Br_3{<}\begin{matrix}C{:}N\\C{:}N\end{matrix}{>}C_6H_4,$$

m. p. 255°, and *tolutribromoresazine*, $C_{16}H_{12}Br_3{<}\begin{matrix}C{:}N\\C{:}N\end{matrix}{>}C_7H_6$, m. p. 275—280°, in the usual way, reacting with ethereal hydrazines to form *tribromoretenequinonephenylhydrazone*, m. p. 245°, and the corresponding p-*nitrophenylhydrazone*, m. p. above 350° (decomp.), *diphenylhydrazone*, $C_{18}H_{13}OBr_3{:}N{\cdot}NPh_2$, m. p. 260—265°, *α-naphthylhydrazone*, m. p. above 300°, *β-naphthylhydrazone*, m. p. above 300° (decomp.), interacting with semicarbazide hydrochloride in boiling acetic acid to form the *semicarbazone*, $C_{16}H_{13}Br_3{<}\begin{matrix}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2\\CO\end{matrix}$, m. p. 280—285°, and yielding with aminoguanidine hydrochloride, *tribromoretenequinoneaminoguanidine hydrochloride*, which decomposes at 218—220°, and yields by treatment with ammonium hydroxide the free *base*, $C_{16}H_{13}Br_3{<}\begin{matrix}CO\\C{:}N{\cdot}NH{\cdot}C(:NH){\cdot}NH_2\end{matrix}$, m. p. 285° (decomp.). By nitration with fuming nitric acid at 0—5°, tribromoretenequinone yields *tribromonitroretenequinone*, $C_{18}H_{12}O_4NBr_3$, m. p. 255°. The following new retene derivatives are described : *toluresazine*, $C_{16}H_{16}{<}\begin{matrix}C{:}N\\C{:}N\end{matrix}{>}C_7H_6$, m. p. 155° ; *retenequinonesemicarbazone*, m. p. 200° ; *retenequinoneaminoguanidine*, and its *hydrochloride*, m. p. 253—254° (decomp.). The reaction between ethereal magnesium

phenyl bromide and an ethereal suspension of retenequinone leads to the formation of *dihydroxydiphenyldihydroretene*, $C_{30}H_{28}O_2$, m. p. 173—174°. C. S.

Influence of Constitution on the Rotatory Power of Optically Active Substances. III. Menthyl Esters of Terephthalic Acid, β-Naphthoic Acid, and Certain of their Reduction Products. Hans Rupe [with F. Münter] (*Annalen*, 1910, 373, 121—128. Compare Abstr., 1903, i, 565; 1909, i, 927).—A comparison of the optical rotatory powers of the menthyl esters of terephthalic acid, β-naphthoic acid, muconic acid (compare Hilditch, Trans., 1909, 95, 1570), benzoic acid, α-naphthoic acid, and of the corresponding hydrogenated acids, the results of which may be summarised as follows:

(1) The menthyl esters of the acids with an ethylene linking in the Δ^2- or βγ-position have roughly the same rotatory power as the corresponding esters of the completely saturated acids.

(2) The reduced benzenoid derivatives are not so optically active as the corresponding benzenoid compounds; similarly, menthyl muconate is far more active than the menthyl ester of αβ-dihydromuconic acid, βγ-dihydromuconic acid, or adipic acid; menthyl $\Delta^{1:4}$-dihydroterephthalate is, however, slightly more active than menthyl terephthalate.

(3) In the muconic, benzoic, and α-naphthoic acid series, the acids with the ethylene linking in the αβ(Δ^1)-position are more active than the corresponding acids with the ethylene linking in the βγ(Δ^2)-position; on the other hand, the optical activities of the menthyl esters of Δ^2-tetrahydroterephthalic acid and Δ^3-dihydro-β-naphthoic acid are greater than those of the corresponding Δ^1-acids.

The following esters are prepared by the action of the acid chloride on menthol in the presence of pyridine; the [α] values refer to 10% chloroform solutions unless otherwise stated: *dimenthyl terephthalate*, $C_{28}H_{42}O_4$, white needles, m. p. 75°, $[\alpha]_D^{20}$ −102·64°; *dimenthyl* $\Delta^{1:4}$*-dihydroterephthalate*, $C_{28}H_{44}O_4$, white needles, m. p. 68°, $[\alpha]_D^{20}$ −104·55°; *dimenthyl* Δ^1*-tetrahydroterephthalate*, $C_{28}H_{46}O_4$, white needles, m. p. 125°, $[\alpha]_D^{20}$ −69·42°; *dimenthyl* trans-Δ^2*-tetrahydroterephthalate*, $C_{28}H_{46}O_4$, small, white needles, m. p. 64°, $[\alpha]_D^{20}$ −76·09°; *dimenthyl* trans*-hexahydroterephthalate*, $C_{28}H_{48}O_4$, slender, white needles, m. p. 132—133°, $[\alpha]_D^{20}$ −74·72°; *menthyl β-naphthoate*, $C_{21}H_{26}O_2$, long, colourless prisms, m. p. 75—76°, $[\alpha]_D^{20}$ −91·30° (in benzene); *menthyl* Δ^2*-dihydro-β-naphthoate*, $C_{21}H_{28}O_2$, colourless, viscid oil, b. p. 218°/10·5 mm., $[\alpha]_D^{20}$ −41·40° (in benzene); *menthyl* Δ^3*-dihydro-β-naphthoate*, an oil which decomposes when heated, $[\alpha]_D^{20}$ −53·14° (in benzene); *menthyl tetrahydro-β-naphthoate*, $C_{21}H_{30}O_2$, colourless, viscid oil, b. p. 218°/11 mm., $[\alpha]_D^{20}$ −53·04° (in benzene). W. H. G.

Artificial Camphor. Eugène Darmois (*Compt. rend.*, 1910, 150, 925—927).—Although commercial artificial camphor shows only feeble optical rotatory power, it is possible to obtain a strongly active, synthetic product by working at low temperatures. Algerian

turpentine (containing α-pinene, $[\alpha]_D$ 50·5°) has been converted into borneol hydrobromide; the magnesium derivative of this yielded a mixture of *d*-borneol and *l-iso*borneol, which, on oxidation with chromic acid in the cold, gave *d*-camphor, identical with the natural product, but contaminated with 7% of *l*-camphor. Under the same conditions, a French turpentine containing 96% of *l*-pinene and 4% of *d*-pinene gave a mixture of *l*-camphor with 10% of *d*-camphor (compare Hesse, Abstr., 1906, i, 376). W. O. W.

Thiocamphorimide. Giuseppe Oddo and Anna Mannessier (*Gazzetta*, 1910, 40, i, 43—51).—*Thiocamphorimide*, $C_8H_{14}<^{CS}_{CS}>NH$, prepared by the action of phosphorus pentasulphide on camphorimide, forms golden-yellow scales or prisms, m. p. 135°, $[\alpha]_D$ +63·29°, which smell faintly of garlic and are tasteless; it has acid properties, and with alkali hydroxides it gives orange-yellow solutions, from which it can be reprecipitated unchanged; it dissolves in cold concentrated sulphuric acid, giving an intense red coloration, but determinations of the molecular weight in sulphuric acid by Oddo and Scandola's method (Abstr., 1908, ii, 353) gave half the theoretical value, so that the nitrogen assumes a basic function, the acid sulphate,

$$C_8H_{14}:[CS]_2:NH_2\cdot HSO_4,$$

being formed. A solution of thiocamphorimide in aqueous-alcoholic potassium hydroxide solution gives precipitates with salts of the following metals: zinc; *lead*, $Pb(C_{10}H_{14}NS_2)_2$; barium; *silver*, $C_{10}H_{14}NS_2Ag$; and mercury(ic). *Benzoylthiocamphorimide*,

$$C_{10}H_{14}NS_2Bz,$$

forms intensely yellow, rhombic crystals, m. p. 156—157°. When thiocamphorimide is boiled with aqueous alkali solution until the evolution of hydrogen sulphide ceases, camphoric acid is obtained as the sole product. When heated in a sealed tube with concentrated ammonium sulphide solution, thiocamphorimide is converted into camphorimide, whilst with sodium hydrogen sulphide, camphoric acid alone is obtained. Oxidation of thiocamphorimide by means of alkaline permanganate yields camphorimide. T. H. P.

Preparation of Terpene Alcohols from Pinene Hydrochloride. Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 219243). The *alcohol*, $C_{10}H_{17}\cdot OH$, is prepared by heating pinene hydrochloride at about 140—160° in the presence of water with freshly prepared mildly basic reagents, such as calcium hydroxide, the oxides or hydroxides of zinc or lead, or the alkali or alkaline earth carbonates, and subsequent extraction and distillation of the product; the new alcohol sublimes at 149—150°, has b. p. 204—206°/760 mm. or 90—100°/20 mm., and is of therapeutic value; when heated with dilute mineral acids, water is eliminated, with the formation of camphene. F. M. G. M

Spanish Oil of Turpentine. Obdulio Fernández (*Anal. Fis. Quim.*, 1909, 7, 442—448).—Turpentine oil, distilled in a current of steam, from the resin of *Pinus Halepensis*, grown in Andalusia, has

$D^{20} = 0{\cdot}859$; $[\alpha]_D$ $-8{\cdot}73°$, and n_D 1·4654. It is thus very different in physical properties from French oil of turpentine. When treated in the usual way with hydrogen chloride, it gives 35—40% of a solid monohydrochloride and 60—65% of a liquid monohydrochloride. The hydrochloride when subjected to Grignard's reaction is converted into a *borneol*, m. p. 115—116°, $[\alpha]_D$ $-10°$ in 5% alcoholic solution, which is not identical with ordinary borneol. The yield is 90% of the theoretical, 10% of a *dihydrodicamphene*, $C_{20}H_{34}$, being also formed. When oxidised with potassium dichromate and sulphuric acid, the borneol gives a camphor, the properties of which are being studied.

The *nitrosochloride* of the pinene, m. p. 95°, does not combine readily with ammonia ; a *nitrolamine* was, however, obtained with difficulty, but could not be crystallised. The *salicylidene* and *furfurylidene* derivatives of the latter are not identical with the compounds described by Leach (Trans., 1907, 91, 1). W. A. D.

Hydrogenation of Turpentine Oil. G. Vavon (*Compt. rend.*, 1910, 150, 1127—1130. Compare this vol., i, 52).—In view of the fact that the α-pinene employed in previous experiments was not a homogeneous substance, the author has repeated them, employing different fractions of commercial turpentine. All the fractions, whether from French, German, or American oils, gave on reduction hydrocarbons having very variable rotatory powers ($[\alpha]_D$ $+23{\cdot}8°$ to $-23{\cdot}8°$), but otherwise having the same physical constants as the liquid obtained from α-pinene. The values for the specific rotations were plotted in the form of curves, and the composition of the products deduced from Biot's law of mixtures. In general, the results are in agreement with those previously obtained, and confirm the conclusions of Darmois (this vol., i, 52) on the composition of turpentine oil. W. O. W.

Liquid Pinene Hydrochloride. Philippe Barbier and Victor Grignard (*Bull. Soc. chim.*, 1910, [iv], 7, 342—350).—In a previous paper (Abstr., 1909, i, 501) the authors applied the method of hydration to the study of the hydrocarbons which accompany natural pinene. In the present communication they have with the same object in view examined the liquid hydrochloride formed to a small extent, along with the solid hydrochloride, when pinene is treated with hydrogen chloride. The results indicate that nopinene may be present in natural pinene to the extent of about 5%.

The liquid hydrochloride, b. p. 79—81°/13 mm., was treated with magnesium turnings in presence of some ethyl bromide, and the magnesium compounds formed oxidised by a current of dry oxygen. On fractionation a neutral portion, b. p. 155—170°, an alcohol fraction, b. p. 170—220°, and a viscous product, $(C_{10}H_{17})_2$, b. p. 183°/14 mm., were obtained. The second fraction alone was examined. It consisted of a mixture of alcohols and hydrocarbons, which were separated by Tschugaeff's process. From the purified alcohols some borneol, derived from solid hydrochloride, present as an impurity in the parent material, was isolated. The residual liquid was not homogeneous, since it furnished a mixture of phenylurethanes, of which extreme fractions had m. p. 91° and 115° (approx.). It was therefore

oxidised with nitric acid, and yielded a liquid ketone consisting apparently mainly of fenchone. It was treated with hydroxylamine, and gave (1) camphoroxime, (2) *l*-fenchoneoxime, and (3) an oxime, m. p. 161—162°, somewhat resembling camphoroxime [monoclinic: $a:b:c=0{\cdot}95:1:0{\cdot}7218$, $\beta=100°39'$ (Zander)]. The last product is the principal substance formed, and for the identification of the ketone yielding it, the mixed ketones were treated by sodamide (Semmler, Abstr., 1906, i, 681) and the resulting amides separated into *l*-dihydrofencholamide, m. p. 94°, *r*-dihydrofencholamide, m. p. 115°, and a third *amide*, m. p. 108°, $\alpha_D=-0°35'$, crystallising in brilliant spangles, and which yielded on hydrolysis an *acid*, b. p. 143°/11 mm. and $\alpha_D-1°24'$ in a 15 cm. tube. At present it is impossible to say whether these derivatives are due to a new ketone or to an optically active racemic form of fenchone.

The results indicate that the liquid pinene hydrochloride contains bornyl chloride, fenchyl chloride, and probably tertiary chlorides, the second of these being propably derived from nopinene.

T. A. H.

Essential Oils. Heinrich Haensel (*Bericht von Heinrich Haensel*, October—March, 1909—1910. Compare Abstr., 1909, i, 815).—The leaves of *Sambucus ebulus* (Herba ebuli) yielded 0·0763% oil, of dark brown colour and unpleasant spicy odour; it had D^{15} 0·8998, acid number 250·9, and ester number 46·0. After saponification the oil developed an odour recalling that of apricots or peaches, probably due to the presence of an alcohol. No phenol was present.

The root of *Ononis spinosa* gave 0·02% of oil, composed of a liquid portion, D^{15} 0·9917, and a solid portion.

"Distilled lime oil" gave the following results: D^{15} 0·8612, acid number 1·8, ester number (one hour) 12·5, and acetyl ester number (0·75 hour) 53·42; limonene was detected as well as *l*-terpineol (compare Burgess and Page, Trans., 1904, **85**, 414) and bisabolene.

Vitex agnus castus seeds furnished 0·47% of oil, D^{15} 0·8960, acid number 7·41, ester number 24·0, acetyl ester number 40·0, having a pungent, spicy odour. It contained a phenol with an empyreumatic odour. On saponification, the odour of the oil became pepper-like, and after acetylation, it lost entirely its unpleasant odour.

Syrian peppermint oil had D^{15} 0·9130, acid number 0·0, ester number (one hour) 22·25, acetyl ester number (one hour) 151·5.

Ylang-ylang oil, prepared by extraction of the flowers with light petroleum, had D_4^{30} 0·940, n_D^{30} 1·4920, ester number 135, acetyl ester number 208.

T. A. H.

Oil of Samphire. Marcel Delépine (*Compt. rend.*, 1910, **150**, 1061—1063.* Compare Abstr., 1909, i, 642; Borde, *ibid.*, i, 945).—Fractionation of over a kilogram of samphire oil has enabled the author to identify limonene, cymene, the methyl ether of thymol, and a *d*-pinene having $[\alpha]_D+47°45'$, in addition to the substances already recognised.

W. O. W.

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 468—473.

Examination of the Solid Constituent of Turpentine from Pinus silvestris, of its Derivatives, and of French Colophony. Stanislaus Leskiewicz (*J. pr. Chem.*, 1910, [ii], 403—420).—Schkateloff has suggested that all the acids, such as abietic acid, pimaric acid, and sylvic acid, obtained from the common resins and turpentines, are identical with, or are simple transformation products of, his α-sylvic acid (*Mon. Sci.*, 22, 217; [ii], 22, 548). This suggestion receives support from the author, who gives the name sapic acid to all the preceding acids. The acid, obtained from different sources, does not form crystalline salts, and its rotatory power is very easily changed by heat. Thus the sapic acid, $C_{20}H_{30}O_2$, obtained by the repeated crystallisation of the resin acids from the turpentine of *Pinus silvestris* from anhydrous acetone, and finally from alcohol and water below 60°, has m. p. 142—144° and $[\alpha]_D^{19}$ −105·3° in alcohol ($c = 9·9296$). The sapic acid, prepared from the colophony of turpentine, has m. p. 145—147° and $[\alpha]_D^{18}$ −35·16° ($c = 10·002$), whilst the sapic acid from the colophony of *Pinus maritima* has m. p. 146—148° and $[\alpha]_D^{19}$ 14·21° ($c = 10·0278$). These acids are easily converted into the sylvic acids, of which *l*-sylvic acid (Schkateloff's β-sylvic acid) has been obtained pure in the following manner. The sapic acid or the crude colophony of *Pinus silvestris* is dissolved in glacial acetic acid, and the hot solution is treated with a few drops of concentrated hydrochloric acid; the crude *l*-sylvic acid, which separates from the cold solution, is purified by means of the crystalline sodium salt. Pure *l*-sylvic acid, $C_{20}H_{30}O_2$, has m. p. 171—172°, $[\alpha]_D^{15}$ −102·85° in alcohol ($c = 10$), and forms crystalline potassium and ammonium salts. *l*-Colophonic acid, $C_{20}H_{30}O_2$, obtained by rapidly distilling the sapic acids, the colophony of *Pinus silvestris* or of *Pinus maritima*, or *l*-sylvic acid, has m. p. 191—192° and $[\alpha]_D^{15}$ −56·13° ($c = 5·0096$); probably it is identical with Klason and Köhler's α-colophonic acid.

C. S.

Composition of Natural Scammony. A. Goris and G. Fluteaux (*Bull. Sci. pharm.*, 1910, Jan., Reprint, 2 pp.).—A specimen of this gum-resin collected by Guigues was found to have the following percentage composition: moisture, 5; ash, 7·18; matter soluble in alcohol (95), 79·82; matter insoluble in alcohol (by difference), 8. 66·7% of the gum-resin was soluble in ether. The specific rotation of the resin soluble in alcohol was α_D −21·47°, and of that soluble in ether −24·26° (compare Guigues, Abstr., 1908, ii, 995). The rather high percentage of ash was due to contamination of the scammony by sand carried by the wind. The ash contained ferric oxide, alumina, silica, and lime. No starch was found in the product.

T. A. H.

Resolution of Racemic Cyanohydrins by Emulsin. Karl Feist (*Arch. Pharm.*, 1910, 248, 101—104).—The author is unable to confirm Auld's statement that an active benzaldehydecyanohydrin is produced directly from benzaldehyde, potassium cyanide, and hydrochloric acid (Trans., 1909, 95, 929).

The production of *l*-benzaldehydecyanohydrin by the action of

emulsin on the *dl*-form (Abstr., 1909, i, 589) has induced the author to examine in a similar manner other cyanohydrins, active forms of which are produced by synthesis in the presence of emulsin (Rosenthaler, Abstr., 1909, i, 622). Success is attained only under suitable conditions of concentration.

dl-Acetaldehydecyanohydrin, 1·8 grams, is added to 5 grams of emulsin in 20 grams of water, and air is passed through the mixture for twenty-four hours; the ethereal extract is evaporated; the solution of the residue in chloroform is distinctly lævorotatory. The solution obtained in a somewhat similar manner from 4 grams of *dl*-cinnamaldehydecyanohydrin is also lævorotatory, but the conditions could not be obtained for the resolution of *dl-iso*butaldehydecyanohydrin. The rotations of the cyanohydrins thus obtained are in the opposite directions to those of the cyanohydrins produced by synthesis in the presence of emulsin. C. S.

Hydrolysis of Amygdalin by Emulsin. Leopold Rosenthaler (*Arch. Pharm.*, 1910, 248, 105—112. Compare Abstr., 1909, i, 74).—The first step in the hydrolysis of amygdalin by emulsin is the formation of dextrose and mandelonitrileglucoside (compare Auld, Trans., 1908, 93, 1276). The latter may then undergo fission either into equal molecular quantities of benzaldehyde, hydrogen cyanide, and dextrose, or into dextrose and benzaldehydecyanohydrin, which then undergoes secondary decomposition. Feist's contention that the latter is the case because *d*-benzaldehydecyanohydrin is obtained (Abstr., 1908, i, 437) is baseless, since benzaldehyde and hydrogen cyanide yield the *d*-cyanohydrin in the presence of emulsin (Abstr., 1908, i, 817). His attempt to support his position by parallel experiments in which emulsin acts on amygdalin and on benzaldehyde, hydrogen cyanide, and dextrose (this vol., i, 123) is equally unfortunate, since the author shows that the results are largely influenced or even reversed by the quality of the emulsin employed.

The author inclines to the view that *d*-benzaldehydecyanohydrin is partly a primary and partly a secondary product of the hydrolysis of amygdalin by emulsin. He shows that hydrogen cyanide is produced within two minutes of the commencement of the hydrolysis, and that therefore all the materials, benzaldehyde, hydrogen cyanide, and emulsin, requisite for the synthetic production of the *d*-cyanohydrin are present in the system. An argument in favour of the primary formation of the *d*-cyanohydrin is the fact that it is still present in the products of hydrolysis even when the hydrogen cyanide has been destroyed by the addition of nickel formate. C. S.

Principles of Atractylis gummifera (Sicilian Masticogna). Francesco Angelico (*Gazzetta*, 1910, 40, i, 403—411. Compare Abstr., 1907, ii, 122, 801).—The valeric acid obtained by the hydrolysis of the poisonous principle of *Atractylis gummifera* is the normal acid, and the carbohydrate also obtained is a hexose, which, with phenylhydrazine, yields phenylglucosazone.

The principle may be detected by the two following reactions: (1) If a crystal of the substance is treated with concentrated sulphuric

acid to which a few drops of formaldehyde solution and then water have been added, it assumes a yellow colour, addition of water then resulting in the formation of a blue coloration at the surface of contact of the two liquids. Further addition of water gives a clear blue liquid, the colour of which persists for some days. The coloration disappears if the liquid is rendered alkaline, but reappears on acidification. This reaction may also be employed for revealing the presence of formaldehyde, and is capable of detecting the aldehyde in a liquid containing 3 drops of the 40% solution per litre. The reaction is not given by other aliphatic aldehydes, but with dextrose a red coloration is obtained. (2) An aqueous solution of an aromatic aldehyde containing a hydroxy- or alkyloxy-group, when added to a sulphuric acid solution of the poisonous principle, gives a coloration which varies with the concentration from magenta-red to cochineal-red, or red with a slight violet tinge. This coloration, which is given by piperonaldehyde, vanillin, opianic acid, or *p*-hydroxybenzaldehyde, is not destroyed by diluting the solution with water, but disappears on addition of alkali, subsequent acidification restoring it. The same coloration is given by furfuraldehyde, cinnamaldehyde, and salicylaldehyde, but with the last two compounds the colour disappears on adding water. In dilute solution, the coloration only causes a weakening of the whole spectrum, but with more concentrated solutions, an absorption band in the green having the mean wavelength 5270 is observed. T. H. P.

Picrotoxin. Francesco Angelico (*Gazzetta*, 1910, 40, i, 391—403). —The author has succeeded in oxidising picrotin so as to obtain α-picrotinic acid alone, instead of the mixture of isomeric acids, $C_{15}H_{18}O_8$, formed when the oxidation is effected by means of alkaline permanganate solution (compare Abstr., 1909, i, 318).

α-Picrotinic acid is a monobasic acid, and forms white crystals, m. p. 245° (decomp.). It is stable towards alkaline permanganate, does not react with hydroxylamine, phenylhydrazine, or ethyl iodide, but gives a complex mixture when treated with chromic acid mixture, and with acetic anhydride yields a syrupy product. Its *calcium* salt and *ethyl* ester, m. p. 194°, were prepared. When heated at its m. p., the acid yields a small proportion of a *substance*, forming white crystals, m. p. 230° (decomp.).

Reduction of α-picrotinic acid by means of hydriodic acid and red phosphorus results in the formation of the monocarboxylic acid, $C_{15}H_{18}O_4$, obtained by Oglialoro and Forte (Abstr., 1892, 349) by the reduction of picrotin; the *silver* salt of this acid was prepared. Oxidation of the acid, $C_{15}H_{18}O_4$, by means of permanganate in alkaline solution yields, according to the proportion of oxidising agent employed, one of the three following dicarboxylic acids: (1) an optically inactive *acid*, $C_{13}H_{14}O_2(CO_2H)_2,\frac{1}{2}H_2O$, which crystallises in shining, white needles, m. p. 188°, has the normal molecular weight in freezing acetic acid, and does not contain a carbonyl group; (2) an *acid*, $C_{13}H_{12}O_6$, which forms white, rhombohedral plates, m. p. about 110°, decomp. at about 125—130°; the *silver* salt was prepared; (3)

the *acid*, $C_{13}H_{12}O_7$, m. p. 175°, which is probably a derivative of malonic acid, and the salts of which, on gentle heating, yield a small proportion of a *substance*, m. p. about 260°; the *silver* salt was prepared.

When α-picrotinic acid is subjected to prolonged boiling with 25% sulphuric acid, it is converted into a pale yellow, oily *ketone*, $C_{14}H_{16}O_4$, which yields an *oxime*, m. p. 208—209° (decomp.), and a *semicarbazone*, m. p. 226° (decomp.), and, on oxidation with acid permanganate solution in the cold, gives a monocarboxylic *acid*, $C_{14}H_{16}O_4$, forming white, silky needles, m. p. 165°, and having the normal molecular weight in freezing acetic acid. Oxidation of this acid by alkaline permanganate solution on a water-bath gives the acid, $C_{13}H_{12}O_6$, m. p. 110°, formed by the oxidation of the acid, $C_{15}H_{18}O_4$ (*vide supra*).

From these results the conclusion is drawn that α-picrotinic acid is represented by the formula $CO_2H\cdot C_{14}H_{14}O_2(OH)_3\cdot O$. T. H. P.

Action of Light on Dyes. Kurt Gebhard (*Zeitsch. angew. Chem.*, 1910, **23**, 820—827).—The author has confirmed the theory (*Zeitsch. angew. Chem.*, 1910, **22**, 2484) that the bleaching of dye solutions or of dyed tissues by light is due to the primary formation of a peroxide of the dye. The peroxide is best detected by acidified potassium iodide and starch, by alkaline potassium permanganate, or by diphenylamine and concentrated sulphuric acid; chromic, molybdic, and titanic acids do not indicate the presence of a peroxide, this fact furnishing one of the author's several arguments against the theory of the primary formation of hydrogen peroxide.

The rays which are most effective in the production of the peroxide are those complementary to the colour of the dye. Blue, violet, and ultraviolet rays exert a decomposing action on the peroxide, or occasion a transference of the active oxygen to unattacked molecules of the dye.

The author utilises Mumm's theory of oxidation in the presence of water (Abstr., 1907, ii, 527), and shows by an electrolytic experiment that the perhydroxyl ions are instrumental in bleaching the dye. C. S.

Advances in Vat Dyes. Rene Bohn (*Ber.*, 1910, **43**, 987—1007). —A survey of recent advances in the field of the vat dyes. A lecture delivered before the German Chemical Society. J. J. S.

Condensation of α- and β-Naphthols with Ethyl Acetoacetate. A. Bacovescu (*Ber.*, 1910, **43**, 1280—1282. Compare Bartsch, Abstr., 1903, i, 648).—The condensation of β-naphthol and ethyl acetoacetate has been carried out in the presence of concentrated sulphuric acid and anhydrous ether. A 30% yield of a β-methylnaphthacoumarin, $C_{10}H_6<\begin{matrix}O\text{---}CO\\ CMe{:}CH\end{matrix}$, is obtained when the sulphuric acid is added gradually to the ice-cold mixture and then the whole kept at the ordinary temperature for twenty days. It crystallises in

colourless needles, m. p. 182—183°, and its solutions in alcohol or concentrated sulphuric acid have a blue fluorescence. It yields a *dibromide*, but this loses hydrogen bromide readily, yielding the *bromo*-derivative, $C_{10}H_6<^{O\text{---}CO}_{CMe:CBr}$, m. p. 148°. The *nitro*-derivative has m. p. 258°.

When α-naphthol is used, a 60% yield of Bartsch's 4-methyl-2-naphthacoumarin is formed, and the same product can be obtained when hydrogen chloride is used as the condensing agent. J. J. S.

Xanthen and Triphenylmethane. Friedrich Kehrmann (*Annalen*, 1910, **372**, 287—355).—A further contribution to the chemistry of xanthen derivatives, being, in the main, an extension of the investigations of the author and Dengler (compare Abstr., 1908, i, 1002; Abstr., 1909, i, 249). The salts of quinolphthalein ethers (compare Green and King, Abstr., 1907, i, 933), unlike those of fluorescein trimethyl ether (compare Kehrmann and Dengler, Abstr., 1909, i, 249), are found to be hydrolysed by water with great rapidity, an observation which led to a study of the phthaleins and benzeins.

The author criticises adversely the views of von Baeyer (compare Abstr., 1905, i, 281), and replies to the objections raised by Kropp and Decker (compare Abstr., 1909, i, 248); further, it is considered probable that the intensely coloured hydrochloride of phenylxanthenol (compare Gomberg and Cone, this vol., i, 55) has the formula (I), and when heated passes, with elimination of hydrogen chloride, either into the colourless carbinol chloride (II) or into the coloured oxonium chloride (III).

(I.)

$O<^{C_6H_4}_{C_6H_4}>CPhCl$
(II.)

$Cl\cdot O<^{C_6H_4}_{C_6H_4}>CPh$
(III.)

The view advanced by Gomberg and Cone (*loc. cit.*), that the salts of the phenylacridols are quinocarbonium salts, is held to be quite untenable.

Fluorescein and resorcinolbenzein are regarded by von Liebig as quadrimolecular complexes (*Naturforscherversammlung*, Salzburg; compare also Abstr., 1909, i, 98). Mol.-wt. determinations by the cryoscopic method, using phenol as the solvent, show that these substances, likewise 3-hydroxymethylfluorone, are undoubtedly unimolecular.

[With Otto Dengler.]—3 : 6-Diacetylamino-9-phenylxanthonium chloride (diacetylphenorosamine chloride) crystallises in flat, reddish-brown needles (compare Abstr., 1908, i, 1002); the *chromate*, orange-red needles; *platinichloride*, brick-red, crystalline powder, and *iodide*, orange-yellow needles, were analysed. The chloride, when treated with dilute aqueous sodium hydroxide, yields a bluish-red *substance*, which is converted by hot water into the carbinol *base*, $C_{25}H_{24}O_4N_2$, crystallising in colourless needles, m. p. 248° (decomp.).

Phenorosamine chloride (3 : 6-*diamino*-9-*phenylxanthonium chloride*),

$CPh\lessdot^{C_6H_3(NH_2)}_{C_6H_3(NH_2)}\gtrdot OCl$, obtained by boiling the diacetyl derivative with hydrochloric acid, crystallises in slender, red needles with a blue reflex, and dissolves in alcohol and water, forming intensely fluorescent solutions; it dyes silk pink with a yellow fluorescence; the *platinichloride* is a vermilion powder.

3-Amino-6-hydroxy-9-phenylxanthonium chloride, $C_{19}H_{14}O_2NCl$, crystallises in brick-red leaflets with a blue reflex; the *platinichloride* is a scarlet, crystalline powder.

Acetylaminophenylfluorone (*loc. cit.*), when acted on by methyl sulphate in hot nitrobenzene, yields *3-acetylamino-6-methoxy-9-phenylxanthonium methyl sulphate*, $CPh\lessdot^{C_6H_3(NHAc)}_{C_6H_3(OMe)—}\gtrdot O\cdot SO_4Me$, crystallising in brick-red needles with a blue reflex; the *aurichloride*, *chromate*, *iodide*, and *platinichloride* are crystalline, orange-yellow powders; the chloride, when hydrolysed by boiling dilute hydrochloric acid, yields *3-amino-6-methoxy-9-phenylxanthonium chloride*, crystallising in long, dark red needles with a green reflex; the *platinichloride*,

$$(C_{20}H_{16}O_2N)_2PtCl_6,$$

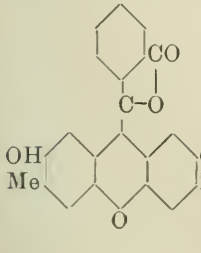
is brick-red.

[With Karl Scheunert.]—The chloride of methyl 3 : 6-dimethoxy-9-phenylxanthonium-2′-carboxylate (compare Abstr., 1909, i, 249) is prepared most readily by the action of hydrogen chloride and methyl alcohol on 3 : 6-dimethoxyfluoran; it crystallises in lemon-yellow leaflets with a blue shimmer, and behaves, according to electrical conductivity measurements, as the chloride of a strong base; the *dichromate*, $(C_{23}H_{19}O_5)_2Cr_2O_7$, long, glistening, orange-red needles, m. p. 138°; *iodide*, red needles; *nitrate*, glistening, yellow leaflets, and *platinichloride*, crystalline, pale orange granules, were prepared.

The *chloride* of the corresponding *ethyl* ester, prepared in a similar manner, forms yellow leaflets with a blue reflex; the violet *iodide*, reddish-orange *bromide*, red *dichromate*, m. p. about 140°, and orange *platinichloride*, $(C_{24}H_{21}O_5)_2PtCl_6$, were prepared.

The *chloride* of *ethyl 3 : 6-diethoxy-9-phenylxanthonium-2′-carboxylate*, similarly prepared from 3 : 6-diethoxyfluoran, forms yellow leaflets with a blue reflex; the *platinichloride*, $(C_{26}H_{25}O_5)_2PtCl_6$, is a crystalline, yellow powder, m. p. 192°; the *bromide* is golden-yellow; the *iodide* is orange-red.

[With Robert Silzer.]—The *methosulphate* of quinolphthalein methyl ester (compare Green and King, Abstr., 1908, i, 1003) is converted by sodium nitrate into the corresponding *nitrate*, which forms yellowish-red crystals, the *platinichloride*, $(C_{23}H_{19}O_5)_2PtCl_6$, is garnet-red.



Toluquinolphthalein (annexed formula) is prepared by heating toluquinol with phthalic anhydride in the presence of stannic chloride; it crystallises in colourless needles, m. p. 298—300°; the *chloride*, $C_{22}H_{17}O_5Cl$, forms red needles, and is converted by hydrogen chloride and methyl alcohol into the *chloride* of the *methyl*

ester, which crystallises in brownish-red needles; the corresponding *platinichloride*, $(C_{23}H_{19}O_5)_2PtCl_6$, forms garnet-red granules.

Dimethyltoluquinolphthalein, prepared by the action of methyl iodide on an alkaline solution of the toluquinolphthalein, forms colourless crystals, m. p. 270° (decomp.); the *salts* are strongly hydrolysed in aqueous solutions; the *chloride* of the corresponding *methyl* ester, $C_{25}H_{23}O_5Cl$, obtained by treating the dimethyl ether with methyl alcohol and hydrogen chloride, crystallises in glistening, orange-red needles, and is hydrolysed very slowly in aqueous solutions; the *platinichloride*, $(C_{25}H_{23}O_5)_2PtCl_6$, is a crystalline, red powder; the *dichromate* forms small, garnet-red needles.

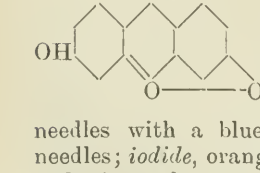
Quinolbenzein chloride, $CPh\langle\begin{smallmatrix}C_6H_3(OH)\\C_6H_3(OH)\end{smallmatrix}\rangle OCl$ (compare von Baeyer, this vol., i, 252), is readily prepared by acting on a solution of quinol and benzaldehyde in glacial acetic acid with concentrated sulphuric acid and oxidising the xanthen derivative thus obtained by means of ferric chloride; the *nitrate*, $C_{19}H_{13}O_3\cdot NO_3$, forms small, glistening, dark red needles; the *dimethyl ether*, $OH\cdot CPh\langle\begin{smallmatrix}C_6H_3(OMe)\\C_6H_3(OMe)\end{smallmatrix}\rangle O$, obtained by treating an alkaline solution of quinolbenzein with methyl iodide, forms colourless crystals, m. p. 143°; the *salts* are hydrolysed to a great degree in aqueous solutions; the *platinichloride*,

$$(C_{21}H_{12}O_3)_2PtCl_6,$$

crystallises in dark red leaflets.

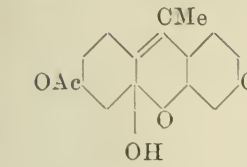
Toluquinolbenzein (2 : 7 - *dihydroxy*-3 : 6 - *dimethyl*-9-*phenylxanthen*-9-*ol*), prepared from toluquinol and benzaldehyde, forms a *chloride*, $C_{21}H_{17}O_3Cl$, crystallising in glistening, brownish-red needles; an aqueous solution of the salt, when treated with sodium hydrogen carbonate, yields a microscopic, crystalline, black *substance*, which is probably a quinhydrone of 1 mol. of the carbinol with 1 mol. of the quinonoid anhydro-base; the *chloride* of the *dimethyl ether* forms glistening, red needles, and is not hydrolysed in aqueous solutions; the *platinichloride*, $(C_{23}H_{21}O_3)_2PtCl_6$, is a crystalline, garnet-red powder.

[With S. M. Jones.]—The *stannichloride* of 3-hydroxymethylfluorone, $(C_{14}H_{11}O_3Cl)_2,SnCl_4$, prepared by heating resorcinol and 2 : 4-dihydroxyacetophenone with stannic chloride at 160—180°, forms large, dark red, glistening granules with a blue metallic reflex, and when treated with an aqueous solution of sodium acetate yields



3-hydroxymethylfluroone (annexed formula), crystallising in large, dark red plates with a blue reflex; the latter substance sinters at 229°, m. p. 238° (decomp.), and forms yellow solutions with an intense green fluorescence; the *chloride*, $C_{14}H_{11}O_3Cl$, forms reddish-yellow needles with a blue reflex; the *platinichloride*, long, lemon-yellow needles; *iodide*, orange-red leaflets; *bromide*, small, orange-red crystals, and *picrate*, lemon-yellow powder, were prepared; the *silver* salt is a brick-red powder. The compound described by Nencki and Sieber as acetylfluorescein (compare Abstr., 1881, 811) is identical with 3-hydroxymethylfluorone. The latter substance, when heated with

acetic anhydride and sodium acetate, yields 3 : 6-diacetoxyxanthone, m. p. 204° (compare Meyer and Conzetti, Abstr., 1897, i, 380), and the *acetyl* derivative of the corresponding xanthonecarbinol (annexed formula), which crystallises in yellow prisms, m. p. 200°. 3-Hydroxymethylfluorone is converted by glacial acetic acid and sodium nitrite into an *oximino*-



derivative, $O<\begin{matrix}O{:}C_6H_3(OH)\\C_6H_3\end{matrix}\!\!>C{\cdot}CH{:}N{\cdot}OH$, which crystallises in stout, dark red prisms with a green, metallic reflex, m. p. 200° (decomp.), and is decomposed quantitatively by aqueous sodium hydroxide into 3 : 6-dihydroxyxanthone and hydrogen cyanide. The reduction of 3 : 6-dihydroxyxanthone with sodium amalgam leads to the formation of *3-hydroxyfluorone*, $O<\begin{matrix}O{:}C_6H_3(OH)\\C_6H_3\end{matrix}\!\!>CH$, a brick-red, crystalline powder with a blue reflex, which commences to darken at 275°, but does not melt at 320°; the solutions exhibit an intense, green fluorescence; the *chloride* forms yellow needles.

[With Xavier Vogt.]—Resorufin methyl ether (compare Nietzki, Dietze, and Mäckler, Abstr., 1890, 156), when acted on by methyl sulphate in nitrobenzene at 100°, yields 3 : 6-*dimethoxyphenazoxonium methosulphate*; the *chloride*, $N<\begin{matrix}C_6H_3(OMe)\\C_6H_3(OMe)\end{matrix}\!\!>OCl$, and *platinichloride*, iridescent, bluish-green leaflets, m. p. 110—115°, were prepared.

3 : 6-*Dimethoxyphenazonium* salts, $N<\begin{matrix}C_6H_3(OMe)\\C_6H_3(OMe)\end{matrix}\!\!>NPh{\cdot}X$, are prepared in the same manner from safranol methyl ether; the *chloride*, small, golden-yellow needles; *bromide*, orange-red leaflets with a blue reflex; *platinichloride*, orange leaflets; *dichromate*, yellowish-brown leaflets; *nitrate*, golden-yellow needles, and *iodide*, orange-red needles, were prepared; an aqueous solution of the bromide, when acted on by silver hydroxide, yields a distinctly alkaline solution of the azonium base, which absorbs carbon dioxide, forming the *carbonate*, obtained in yellow needles by evaporating the solution over concentrated sulphuric acid. W. H. G.

Thio-γ-pyrone Derivatives. Hermann Apitzsch and C. Kelber (*Ber.*, 1910, **43**, 1259—1266. Compare Abstr., 1909, i, 48).—Sodium chloroacetate has been substituted for ethyl chloroacetate in the condensations with ethyl 2 : 6-dithiol-4-ketopenthiophen-3 : 5-dicarboxylate, and products similar to those already described have been obtained.

3 : 5-*Dihydroxy-4-ketopenthiophendithiophen*,

$$OH{\cdot}C_4SH<\begin{matrix}CO\\S\end{matrix}\!\!>C_4SH{\cdot}OH,$$

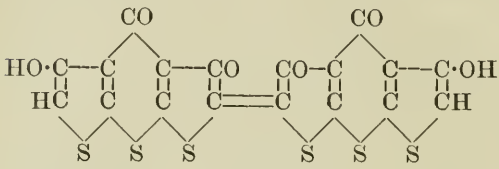
is formed by condensing the dithiol with sodium carbonate, sodium chloroacetate, and a little water for fifteen minutes at 60—70°, then allowing to cool, adding 10*N*-sodium hydroxide solution, warming to 50°, and finally adding acetic acid. It crystallises in brownish-yellow,

slender needles or in golden-yellow prisms, m. p. 255° (decomp.). The *diacetyl* derivative, $C_{13}H_8O_5S_3$, forms colourless, glistening needles, m. p. 174°.

Ethyl 3-*hydroxy*-6-*thiol*-4-*ketopenthiophenthiophen*-5-*carboxylate*,

$$\begin{array}{l} CO_2Et\cdot C\cdot CO\cdot C{-}{-}C\cdot OH \\ \quad\;\; \| \quad\;\; \| \quad\;\; \| \\ \quad HS\cdot C{-}S{-}C\cdot S\cdot CH \end{array},$$

is formed when a much smaller amount of sodium chloroacetate is used. It crystallises in orange-red prisms or yellow needles, m. p. 174·5° (decomp.).



Bis-5-*hydroxy*-4-*ketopenthiophendithiophen* (annexed formula) is obtained in the form of its mono- or di-potassium salt when the dihydroxyketopenthiophendithiophen is oxidised with ammonium persulphate in potassium hydroxide solution or with potassium ferricyanide. The salts form black, amorphous powders, and when decomposed with mineral acids yield the free compound, $C_{18}H_4O_6S_6$, as a black powder.

Chloroacetone condenses with the dithiol in the same manner as sodium chloroacetate, and it is easy to obtain a theoretical yield of the intermediate product, *ethyl* 4-*keto*-2 : 6-*dithiolacetonylpenthiophen*-3 : 5-*dicarboxylate*, $CO<\begin{matrix}C(CO_2Et):C(S\cdot CHAc)\\C(CO_2Et):C(S\cdot CHAc)\end{matrix}>S$, as glistening, colourless needles, m. p. 77°, which yield 3 : 5-*dihydroxy*-2 : 6-*diacetyl*-4-*ketopenthiophendithiophen*, $C_9OS_2(OH)_2Ac_2$, when warmed with alkalis. The dihydroxy-compound crystallises in pale yellow needles, which decompose at 300°, and yields a *tri-phenylhydrazone*, $C_{31}H_{26}O_2N_6S_3$, in the form of red plates, decomposing at 261°.

Ethyl 2-*acetyl*-3-*hydroxy*-6-*thiol*-4-*ketopenthiophenthiophen*-5-*carboxylate*,

$$\begin{array}{l} CO_2Et\cdot C\cdot CO\cdot CH{-}{-}C\cdot OH \\ \quad\;\; \| \quad\;\; \| \\ \quad SH\cdot C{-}S\cdot CH\cdot S\cdot CAc \end{array},$$

obtained when a smaller amount of chloroacetone is used, crystallises in orange-yellow needles, m. p. 143—144°.

Bromoacetophenone also condenses with the dithiol, yielding *ethyl* 4-*ketopenthiophen*-2 : 6-*dithiolacetophenone*-3 : 5-*dicarboxylate*,

$$CO<\begin{matrix}C(CO_2Et):C(S\cdot CH_2\cdot COPh)\\C(CO_2Et):C(S\cdot CH_2\cdot COPh)\end{matrix}>S,$$

as pale yellow plates, m. p. 142—143°; with alkalis it yields 3 : 5-*dihydroxy*-2 : 6-*dibenzoyl*-4-*ketopenthiophendithiophen*,

$$C_9OS_3(OH)_2(COPh)_2,$$

which crystallises in deep yellow plates, m. p. 245°.

Ethyl 2-*benzoyl*-3-*hydroxy*-6-*thiol*-4-*ketopenthiophenthiophen*-5-*carboxylate*, $C_{17}H_{12}O_5S_3$, crystallises in orange-red, glistening needles, m. p. 157°. J. J. S.

[Preparation of Halogen "Thioindigos" (Bisoxythionaphthens).] Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 219268).—When "6 : 6'-diethoxythioindigo" dissolved in sulphuric acid containing anhydride is treated with bromine, a

"*dibromo*-6 : 6′-*diethoxythioindigo*" is obtained. When chlorine is employed, a "*chloro*-6 : 6′-*diethoxythioindigo*" is formed.

F. M. G. M.

Oxidation Products of "Thioindigo." Negoita Danaïla (*Bull. Soc. chim.*, 1910, [iv], 7, 359—361. Compare Abstr., 1908, i, 987; 1909, i, 251).—When "thioindigo," suspended in acetic acid, is oxidised by nitric acid (94%), three *substances* are produced: $C_{16}H_8O_3S_2$, m. p. about 325° (decomp.); $C_{16}H_8O_4S_2$, m. p. 245° (decomp.), and $C_{16}H_8O_5S_2$, m. p. 237° (decomp.). The first crystallises from xylene, and the other two from nitrobenzene. All three are red, and possess properties similar to those of "thioindigo"; they are reduced by sodium hyposulphite and by zinc and acetic acid, forming colourless substances. Their solutions in sulphuric acid are blue or bluish-green, but become reddish-violet for the first two, and orange for the third on dilution. In xylene solution the first shows an absorption band at $\lambda = 539$, the second at $\lambda = 537$, and the third at $\lambda = 487{\cdot}7$. The first and third also show bands at $\lambda = 497{\cdot}5$ and $\lambda = 494$ respectively. T. A. H.

The Alleged Formation of Adrenaline from Tyrosine. A. J. Ewins and P. P. Laidlaw (*J. Physiol.*, 1910, 40, 275—278).—No evidence of the formation of adrenaline from tyrosine or from *p*-hydroxyphenylethylamine and dihydroxyphenylethylamine was found. Halle's experiments in this direction are criticised. W. D. H.

The Adrenaline Series. Carl Mannich (*Arch. Pharm.*, 1910, 248, 127—171. Compare Abstr., 1909, i, 321; this vol., i, 167).—The reaction between methylamine and chloro- or bromo-hydrins of the types: $CH_2<^{O}_{O}>C_6H_3\cdot CH(OH)\cdot CH_2Br$ and

$$C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2Br$$

is more complex than Barger and Jowett (Trans., 1905, 87, 967) and Pauly and Neukam (this vol., i, 96) suppose. A mere replacement of the halogen by the methylamino-group does not occur. An unstable oxide is first formed, which reacts with a second molecule of methylamine to form bases of the adrenaline series (I) and of the *iso*adrenaline series (II); for example, $C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2Br \xrightarrow{NH_2Me} C_6H_3(OMe)_2\cdot CH<^{O}_{CH_2} \xrightarrow{NH_2Me}$ (I) $C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2\cdot NHMe$ and (II) $C_6H_3(OMe)_2\cdot CH(NHMe)\cdot CH_2\cdot OH$. The constitution of the side-chain is of importance in determining the proportions of the two bases obtained, because *iso*safrolebromohydrin and *iso*eugenol methyl ether bromohydrin yield only the bases of the *iso*-series (II); in these two cases, the intermediately formed oxides are stable, and can be isolated. Bases of the *iso*-series can be dealkylated by hydriodic acid, yielding products of very feeble physiological activity. Bases of the adrenaline series are also dealkylated, but at the same time the methylamino-group is displaced, as is the case with adrenaline itself, by treatment with mineral acids. The dibromides of 3 : 4-methylenedioxystyrene, 3 : 4-dimethoxystyrene, and similar substances readily suffer replacement of the α-halogen atom by a methoxy-

group by treatment with boiling methyl alcohol, and the resulting methoxy-bromide reacts with alcoholic methylamine in the sense: $\cdot CH(OMe)\cdot CH_2Br + 2NH_2Me = \cdot CH(OMe)\cdot CH_2\cdot NHMe + NH_2Me,HBr$.

Unfortunately, however, the dealkylation of these compounds by hydriodic acid is also accompanied by the elimination of methylamine.

[With P. Neumann.]—The following series of reactions lead to a satisfactory yield of 3 : 4-dimethoxystyrene. Veratrole, which is obtained almost quantitatively from guaiacol and methyl sulphate in alkaline solution, is converted by aluminium chloride and acetyl chloride in carbon disulphide at 0° into acetoveratrone (3 : 4-dimethoxyacetophenone), b. p. 286—288° or 158°/9 mm. (not 205°/10 mm., as given in the literature), which readily dissolves in ice-water and separates almost completely by warming, and forms an *oxime*, m. p. 140°, and a *semicarbazone*, m. p. 211° (decomp.). Acetoveratrone is reduced by sodium amalgam and alcohol to the *pinacone*,

$$C_6H_3(OMe)_2\cdot CMe(OH)\cdot CMe(OH)\cdot C_6H_3(OMe)_2,$$

m. p. 169°, and by sodium and alcohol to 3 : 4-*dimethoxyphenylmethyl carbinol*, $C_6H_3(OMe)_2\cdot CHMe\cdot OH$, b. p. 156—160°/9 mm., which forms an *acetate*, b. p. 156—158°/8 mm., and a *chloride*, m. p. 65—67°, from which the *ethyl ether*, $C_6H_3(OMe)_2\cdot CHMe\cdot OEt$, b. p. 132°/8 mm., is obtained by the action of alcoholic sodium ethoxide, and 3 : 4-dimethoxystyrene by boiling pyridine.

α-3 : 4-Dimethoxy-β-bromo-α-hydroxyethylbenzene, obtained from 3 : 4-dimethoxystyrene by Barger and Jowett's method (*loc. cit.*), yields after two to three days' interaction at 0° with 33% alcoholic methylamine a mixture of the two bases (I and II) (above), which is separated by means of the insolubility of the hydrochloride of (II) in acetone. iso*Adrenaline dimethyl ether* (formula II), m. p. 63—64°, crystallises from anhydrous ether, forms a *hydrochloride*,

$$C_{11}H_{17}O_3N,HCl,$$

m. p. 178, and yields by boiling with hydriodic acid, D 1·68, methyl iodide and a viscous liquid, which probably contains *iso*adrenaline, since a very dilute aqueous solution responds to the catechol reaction with ferric chloride. *Adrenaline dimethyl ether* (formula I), m. p. 104°, b. p. 196°/13 mm., separates from ethyl acetate in leaflets, does not yield crystalline salts, and suffers profound degradation by treatment with boiling hydriodic acid, resinous products and methylamine being formed.

3 : 4-Dimethoxystyrene dibromide and boiling methyl alcohol produce 3 : 4-*dimethoxy-β-bromo-α-methoxyethylbenzene*,

$$C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2Br,$$

an oily liquid which is decomposed by distillation, yielding ω-bromo-3 : 4-*dimethoxystyrene*, $C_6H_3(OMe)_2\cdot CH{:}CHBr$, m. p. 65°, and reacts with 33% alcoholic methylamine at 110° for ten hours to form *adrenaline trimethyl ether*, $C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2\cdot NHMe$, b. p. 164—166°/12 mm., the *hydrochloride* of which has m. p. 182°, and the *hydriodide*, m. p. 163—164°. The decomposition of the trimethyl ether by hydriodic acid results in the formation of methyl iodide, methylamine, and resinous products.

3 : 4-Dimethoxy-β-bromo-α-methoxyethylbenzene reacts in a similar

way with 33% alcoholic dimethylamine to form *N-methyladrenaline trimethyl ether*, $C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2\cdot NMe_2$, b. p. 155—156°/9 mm. (*hydrochloride*, m. p. 175°), and with saturated alcoholic ammonia to form *arterenol trimethyl ether*, $C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2\cdot NH_2$, b. p. 164—167°/12 mm. [*hydrochloride*, m. p. 167° (decomp.); *platinichloride*, decomposing at 160°].

[With W. Jacobsohn.]—The reaction between *iso*eugenol methyl ether bromohydrin and 13% alcoholic methylamine for two days leads to the formation of β-methyl*iso*adrenaline dimethyl ether,

$$C_6H_3(OMe)_2\cdot CH(NHMe)\cdot CHMe\cdot OH,$$

m. p. 63, which forms a *hydrochloride*, m. p. 205°, insoluble in acetone, and is converted by hydriodic acid into β-methyl*iso*adrenaline, $C_6H_3(OH)_2\cdot CH(NHMe)\cdot CHMe\cdot OH$. [These compounds have been described previously as β-methyladrenaline dimethyl ether and β-methyladrenaline respectively (Abstr., 1909, i, 321).] This base, like others of the *iso*-series, is stable to boiling mineral acids, and exhibits very slight physiological activity.

The reaction between 3 : 4-methylenedioxy-β-bromo-α-hydroxyethylbenzene and 10% alcoholic methylamine for three days leads to the formation of two bases, iso*adrenaline methylene ether*,

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH(NHMe)\cdot CH_2\cdot OH,$$

m. p. 81°, the *hydrochloride* of which, m. p. 166—168°, is insoluble in acetone, and *adrenaline methylene ether*,

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH(OH)\cdot CH_2\cdot NHMe,$$

m. p. 95—96°.

An aqueous alcoholic mixture of the preceding bromohydrin and dimethylamine yields a viscous liquid, b. p. 180—190°/16 mm., which probably consists of a mixture of the two bases,

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH(OH)\cdot CH_2\cdot NMe_2$$

and $CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH(NMe_2)\cdot CH_2\cdot OH$, one of which (probably the second), m. p. 88—89°, b. p. 185—186°/16 mm., can be separated as the *hydrochloride*, m. p. 185—186°, from the solution of the mixture in alcohol. The presence of the first base in the mixture is indicated by treating a benzene solution of the liquid with sodium, and subsequently with methyl iodide, at 100° for five hours, whereby a *methiodide*, $CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH(OMe)\cdot CH_2\cdot NMe_3I$, m. p. 244° (decomp.), is obtained by repeated crystallisation of the product from alcohol, identical with that described below.

3 : 4-Methylenedioxystyrene dibromide is converted by boiling methyl alcohol into 3 : 4-*methylenedioxy-β-bromo-α-methoxyethylbenzene*, $CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH(OMe)\cdot CH_2Br$, b. p. 167—170°/4 mm. (with partial decomp.), which is converted by 33% alcoholic methylamine at 110° for ten hours into the *methyl ether* of adrenaline methylene ether, $CH_2\langle{}^{O}_{O}\rangle C_6H_3\cdot CH(OMe)\cdot CH_2\cdot NHMe$, b. p. 175—178°/25 mm.

(*hydrochloride*, m. p. 159—160°), and by 33% alcoholic dimethylamine in a similar manner into the *methyl ether* of *N*-methyladrenaline methylene ether, $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3\cdot CH(OMe)\cdot CH_2\cdot NMe_2$, b. p. 150°/16 mm. (*hydrochloride*, m. p. 206°). By the addition of methyl iodide to the latter base, a *methiodide*, m. p. 244° (decomp.), is obtained, identical with that mentioned above.

A base, probably *β-methyliso adrenaline methylene ether*, $CH_2O_2:C_6H_3\cdot CH(NHMe)\cdot CHMe\cdot OH$, m. p. 66°, b. p. 186°/17 mm. [*hydrochloride*, m. p. 225—226° (decomp.)], is obtained by shaking *β*-bromo-*α*-hydroxydihydro*iso*safrole and aqueous methylamine for fifty hours or by heating *iso*safrole oxide and 33% alcoholic methylamine at 100° for six hours. *Nβ-Dimethyliso-adrenaline methylene ether*, $CH_2O_2:C_6H_3\cdot CH(NMe_2)\cdot CHMe\cdot OH$, m. p. 66—68°, b. p. 175—176°/15 mm. (*hydrochloride*, m. p. 212°), is obtained by the interaction of the preceding *iso*safrole bromohydrin and 33% alcoholic dimethylamine in aqueous alcohol for two days at the ordinary temperature.

β-Bromo-*α*-methoxydihydro*iso*safrole (Hoering, Abstr., 1905, i, 903) and 33% alcoholic methylamine, reacting at 120° for six hours, yield the *methyl ether* of *β*-methyladrenaline methylene ether, $CH_2O_2:C_6H_3\cdot CH(OMe)\cdot CHMe\cdot NHMe$, b. p. 159—160°/14 mm., the *hydrochloride* of which has m. p. 202° (decomp.). C. S.

Angostura Alkaloids. Julius Tröger and O. Müller (*Arch. Pharm.*, 1910, **248**, 1—22. Compare Beckurts and Frerichs, Abstr., 1906, i, 34).—Extr. angostur. æther (Merck) is mixed with its own volume of ether, and repeatedly treated with 20% acetic acid until the aqueous layer is only faintly yellow. The aqueous extracts are treated with concentrated sulphuric acid so long as sulphates are precipitated. These are collected, the bases are liberated by ammonium hydroxide, and are recrystallised from alcohol until the m. p. is 95°. The product is then separated by petroleum into an insoluble basic mixture *A*, and a solution from which cusparine and a fraction, m. p. 106—150°, are obtained.

The filtrate from the sulphates yields with concentrated hydrochloric acid a yellow salt, from which a base, probably galipidine, is isolated. The hydrochloric acid filtrate is basified with ammonium hydroxide, the reddish-brown, viscous product is treated with dilute sulphuric acid, the resulting sulphates are purified by crystallisation, and the liberated bases are recrystallised from alcohol, whereby galipine is obtained in a good yield.

The basic mixture *A* is separated by alcohol into cusparine, galapine, and a new, very sparingly soluble alkaloid, m. p. 233°.

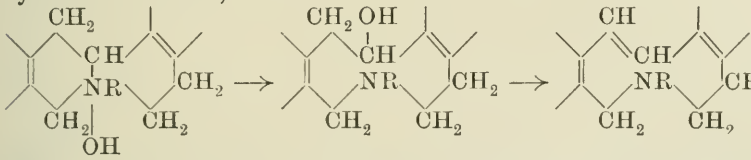
The ethereal solution of the original extract, after its treatment with 20% acetic acid, is repeatedly extracted with dilute sulphuric acid; the bases are liberated from the acid extracts, and are purified from petroleum, whereby a good yield of cusparine is obtained.

Galipine, $C_{20}H_{21}O_3N$, m. p. 115—115·5°, contains three methoxy-

groups, and yields veratric and anisic acids, a small quantity of an amine, and an acid, m. p. 241—247°, containing nitrogen (cinchomeronic acid?) by oxidation with potassium dichromate and sulphuric acid; the oxidation of galipine sulphate by potassium permanganate in neutral solution at 40—50° yields a very small amount of veratric acid, an *acid*, $C_8H_7O_6N$, m. p. 244—246°, and another acid containing nitrogen, m. p. 262—264°. When the oxidation of the galipine sulphate by potassium permanganate is not carried to completion, but is interrupted when all the galipine has been oxidised, the products of oxidation are found to consist of veratric acid, together with acids, m. p. 191·5°, 165—166°, 188—189·5°, the amounts of which are too small for their satisfactory examination.

The oxidation of galipidine by potassium dichromate and sulphuric acid yields a mixture of two aromatic acids (one of which probably is veratric acid), a base, m. p. 138°, formic acid, and a liquid with the odour of pyridine; the available amount of galipidine, however, was too small for the satisfactory examination of these products. C. S.

Isomerism of the Ammonium Compounds Derived from Tetrahydroberberine. Arthur Voss and Julius Gadamer (*Arch. Pharm.*, 1910, **248**, 43—80).—The recognition of berberine as an *iso*quinoline derivative makes it permissible to conceive that the strongly basic ammonium hydroxides obtained by the action of silver oxide on tetrahydroberberine alkyl iodides may undergo transformation into feebly basic carbinol bases, from which anhydro-bases could result by the loss of water, thus:



The hydroxyl group of the ammonium base can evidently migrate to any one of the three neighbouring carbon atoms, but the depicted formula of the carbinol base is the only one that accounts for the production of an optically inactive anhydro-base. The carbinol base has not been isolated; the authors show, however, that the theory serves to reconcile many of the conflicting observations of Schmidt and his co-workers on the alkyl iodide additive compounds of tetrahydroberberine.

Tetrahydroberberine contains an asymmetric carbon atom, and also a neighbouring nitrogen atom, which is attached to three different groups. By the addition of an alkyl iodide, therefore, two diastereoisomeric quaternary iodides should result. This is the case, for *d*- and *l*-canadines (the resolution products of tetrahydroberberine) yield each a pair of ethiodides, d-*α-canadine ethiodide*, $C_{22}H_{26}O_4NI,1\frac{1}{2}H_2O$, m. p. 187°, $[\alpha]_D^{20}$ +92·2° in alcohol, and d-*β-canadine ethiodide*, m. p. 225°, $[\alpha]_D^{20}$ +115·0°, and the corresponding l-*α-compound*, m. p. 187°, $[\alpha]_D^{20}$ −91·5°, and l-*β-compound*, m. p. 225°, $[\alpha]_D^{20}$ −115·3°. r-*α-Canadine ethiodide*, $C_{22}H_{26}O_4NI,\frac{1}{2}H_2O$, has m. p. 187°, and the r-*β-compound*, $C_{22}H_{26}O_4NI,1\frac{1}{2}H_2O$, has m. p. 240°; a mixture of equal quantities

of the two substances, after being crystallised from 70% alcohol, is identical with tetrahydroberberine ethiodide, m. p. 229—230°. The *α-canadine ethochlorides* crystallise in small, yellow crystals containing $2H_2O$, and have m. p. 233°; the *d*-form has $[\alpha]_D^{20}$ +128·3°, and the *l*-form has $[\alpha]_D^{20}$ −127·3°; the racemic modification also has m. p. 233°. The *β-canadine ethochlorides*, m. p. 245°, contain $2H_2O$; the *d*-form has $[\alpha]_D^{20}$ +138·5°, and the *l*-form, $[\alpha]_D^{20}$ −138·8°; the racemic modification has m. p. 260°. The corresponding *ethonitrates* are also described. The α-compounds are converted into the β-compounds by heating in the absence of air.

The action of silver oxide on tetrahydroberberine ethiodide in 50% alcohol, or of barium hydroxide on *tetrahydroberberine ethyl hydrogen sulphate*, m. p. 270°, yields the corresponding ammonium base, which, however, cannot be isolated free from the carbonate.

The *ethyl anhydro-base* of tetrahydroberberine, $C_{20}H_{20}O_4NEt$, m. p. 132·5°, is obtained by heating tetrahydroberberine ethyl carbonate in hydrogen for seventeen and a-half hours, treating the solution of the product in very dilute hydrochloric acid with ammonium hydroxide, and extracting the precipitate with ether; it has only a slight alkaline reaction, is reconverted into the quaternary ammonium base by boiling alcohol, and forms a *hydrochloride*, m. p. 185°, *nitrate*, m. p. 165—166°, and *hydrogen sulphate*, m. p. 260°.

l-α- and β-Canadine methiodides, obtained from *l*-canadine and an excess of ethyl iodide, are converted, in alcoholic solution, into the hydroxides; the solution is evaporated in a current of hydrogen, the residue is dissolved in dilute hydrochloric acid, and the solution, after treatment with ammonium hydroxide, is extracted with ether; the residue obtained from the ethereal solution is purified from acetone, and consists of the anhydro-base, m. p. 132·5°, which is quite inactive optically. The ammoniacal mother liquor contains β-tetrahydroberberine ethochloride, m. p. 257°, which appears to be identical with *r*-β-canadine ethochloride, and also with Link's tetrahydroberberine ethochloride (Abstr., 1892, 1499); the nitrates of the three bases also correspond. C. S.

Nature of the So-called Double Salts formed by Caffeine with Alkali Salts. Giovanni Pellini (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 329—333).—In order to ascertain whether the substances obtained by dissolving caffeine in concentrated aqueous solutions of salts of the alkali metals and evaporating the liquid to dryness at a gentle heat are definite double salts or merely mixtures, the author has investigated the mutual solubility relations of caffeine and sodium benzoate. The solubility of caffeine in water is increased considerably by the addition of the benzoate, which also exhibits increased solubility, but to a less degree. The solubility curves at 25° and at 40° indicate that these two compounds do not unite to form a compound capable of existence in the solid state. T. H. P.

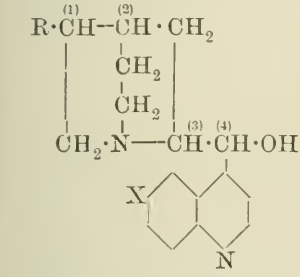
Existence in Solution of Compounds of Caffeine and Sodium Benzoate. Giovanni Pellini and Mario Amadori (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 333—338. Compare preceding abstract).—The authors have measured the variations produced in the freezing

points of solutions of sodium benzoate of a number of different, fixed concentrations by the addition of increasing quantities of caffeine. With all the sodium benzoate solutions, abnormal changes in the freezing point were observed. With the more dilute solutions, the presence of caffeine lowers the freezing point, but by less than the calculated amount; in the case of solutions of medium concentration, the freezing points are not changed, whilst with more concentrated solutions, rises of the freezing points are produced by addition of caffeine. It is hence evident that in solution caffeine and sodium benzoate form a compound (probably by the union of the caffeine with the benzoic ion to form a complex caffeinebenzoic ion) which undergoes dissociation in dilute solution.

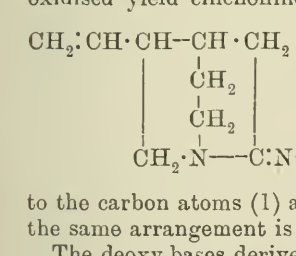
The addition of mannitol, dextrose, or aniline to solutions of sodium benzoate produces normal depressions of the freezing points.

T. H. P.

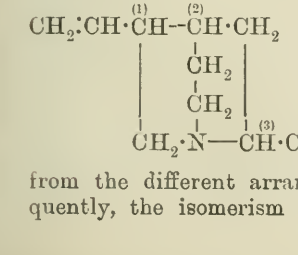
Cinchona Alkaloids. XII. Paul Rabe [with Erich Kuliga, Oswald Marschall, Wilhelm Naumann, and William F. Russell] (*Annalen*, 1910, 373, 85—120. Compare Abstr., 1909, i, 252, 407, 408).—The configurations of cinchonine, cinchonidine, quinine, quinidine, and hydrocinchonine may be represented by the annexed formula; in the first two alkaloids, R = $-CH{:}CH_2$ and X = H; in quinine and quinidine, R = $-CH{:}CH_2$ and X = OMe; in hydrocinchonine, R = Et and X = H; for the purpose of discussing the stereochemical relationship of these alkaloids, the four asymmetric carbon atoms are numbered in the manner indicated.



It has been shown (*loc. cit.*) that cinchonine and cinchonidine when oxidised yield cinchoninone, whilst quinine and quinidine give rise to quininone; these two ketones are decomposed when acted on by amyl nitrite, yielding α-oximino-β′-vinylquinuclidine (annexed formula); it is now found that the preparations of this substance from the four alkaloids are optically identical, showing that these alkaloids with regard to the carbon atoms (1) and (2) have the same spacial configuration; the same arrangement is probably present also in hydrocinchonine.



The deoxy-bases derived from cinchonine and cinchonidine, likewise from quinine and quinidine, are structurally identical, but differ from one another in optical properties; since there are three asymmetric carbon atoms present in the molecule of these compounds (annexed formula), of which the spacial arrangement of (1) and (2) in each case has been shown to be identical, it follows that the isomerism results from the different arrangement of the substituents on (3); consequently, the isomerism of cinchonine and cinchonidine, likewise of



quinine and quinidine, must also be occasioned by the mirror-image arrangement of the substituents on the carbon atom (3).

The formation of cinchotoxine (cinchonicine) from cinchonine and cinchonidine is accompanied by the destruction of the asymmetry of the carbon atoms (3) and (4); hence the formation of the same compound from the stereo-isomerides. Similarly, quinine and quinidine give rise to only one compound, namely, quinotoxine (quinicine).

The reason why only one ketone is obtained from quinine and quinidine, also from cinchonine and cinchonidine, has been discussed already (compare Abstr., 1909, i, 252); the present communication contains the results of a careful investigation of the mutarotation of quininone and cinchoninone.

Measurements of the optical rotatory powers of solutions of the cinchona alkaloids are cited, which show that they do not change with time. The following values of $[\alpha]_D$ are recorded; unless otherwise stated, the solvent is 99% alcohol: cinchonine, $[\alpha]_D^{23}$ +224° (c = 0·606 at 20°); cinchonine hydrochloride, $[\alpha]_D^{25}$ +133° (c = 1·407 at 20° in chloroform); cinchonidine, $[\alpha]_D^{11}$ −111° (c = 0·878); quinine, $[\alpha]_D^{15}$ −158° (c = 2·136 at 15°); quinidine, $[\alpha]_D^{15}$ +243·5° (c = 0·7735 at 15°); hydrocinchonine, $[\alpha]_D^{14}$ +190° (c = 0·406 at 12°); cinchonine chloride ($2H_2O$), $[\alpha]_D^{13}$ +49·77° (c = 2·009), anhydrous, m. p. 110°, $[\alpha]_D^{13}$ +55·7° (c = 1·975); cinchonine chloride hydrochloride, $[\alpha]_D^{24}$ +49·5° (c = 1·5555 in water); cinchonidine chloride, $[\alpha]_D^{13}$ +78·2° (c = 2·020); cinchonidine chloride hydrochloride, $[\alpha]_D^{24}$ +24·16° (c = 1·573 in water); quinine chloride, $[\alpha]_D^{15}$ +60·36° (c = 1·9465); quinidine chloride, $[\alpha]_D^{15}$ +35·25° (c = 1·943); deoxycinchonine, $[\alpha]_D^{13}$ +179·3° (c = 2·025), +194·3° (c = 2·030 in chloroform); deoxycinchonidine, $[\alpha]_D^{13}$ −29·9° (c = 2·006), −19·7 (c = 2·006 in chloroform); deoxyquinine ($2H_2O$), $[\alpha]_D^{15}$ −93·0° (c = 2·252), anhydrous, $[\alpha]_D^{20}$ −97·7° (c = 2·021); deoxyquinidine ($2H_2O$), $[\alpha]_D^{15}$ +191·9° (c = 2·254), anhydrous, $[\alpha]_D^{20}$ +211·1° (c = 2·023); oximinovinylquinuclidine, $[\alpha]_D^{16}$ +113° (c = 2·005).

Although cinchotoxine (cinchonicine) contains the group $-CH_2\cdot CO-$, it does not exhibit mutarotation; $[\alpha]_D^{18}$ +49·62° (c = 2·684 at 20°). The following values refer to the rotation of the solution when equilibrium has been established: cinchoninone, $[\alpha]_D^{20}$ +76·1° (c = 3·302), +76·9° (c = 1·652); various specimens of cinchoninone hydrochloride were found to differ in the initial optical rotatory power, but all gave the final value $[\alpha]_D^{14}$ +66·4° (c = 1·656 in water), +166·6° (c = 1·656 in chloroform); quininone, $[\alpha]_D^{20}$ +75·5° (c = 2·000); hydrocinchoninone, $[\alpha]_D^{20}$ +76·4° (c = 2·296). W. H. G.

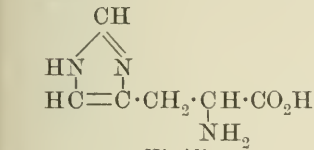
Solubility of Alkaloids of Cinchona Bark and their Salts in Water at 25°. George L. Schaefer (*Amer. J. Pharm.*, 1910, 82, 175—178).—The solubilities of quinine, cinchonidine, cinchonine, and quinidine and of a large number of their salts are given. The results were obtained by determining the parts of water at 25° necessary to dissolve one part of the alkaloid or salt, in order to avoid the difficulty due to the decomposition of the salt by the action of water.

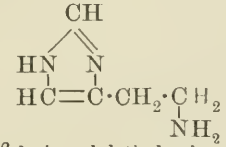
T. A. H.

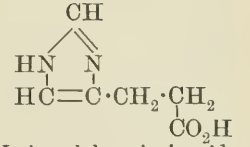
Corydalis Alkaloids. Johannes Gadamer (*Arch. Pharm.*, 1910, 248, 204—206).—With the acceptance of Dobbie and Lauder's

formula for corydaline (Trans., 1902, 81, 148), the author considers that the study of the chemistry of the corydaline sub-group of the corydalis alkaloids may now be replaced by that of the corycavine and bulbocapnine sub-groups (Abstr., 1905, i, 462). He has already proved that bulbocapnine, corydine, and corytuberine contain the ring system of *apo*morphine, and has converted corytuberine into corydine. C. S.

Bacterial Cleavage of Histidine D. Ackermann (*Zeitsch. physiol. Chem.*, 1910, 65, 504—510).—If histidine undergoes anaërobic bacterial cleavage due to the addition of a little putrefying pancreas, the product obtained may be β-iminazolylethylamine if carbon dioxide is split off; the obtaining of this substance proves that the amino-group of histidine is in the α-position to the carboxyl group, a point previously uncertain. It also may undergo the change into iminazolylpropionic acid.


Histidine.


β-Iminazolylethylamine.


Iminazolylpropionic acid.

W. D. H.

Nupharine. A. Goris and L. Crété (*Bull. Sci. Pharm.*, 1910, Jan., Reprint, 3 pp.).—This alkaloid, $C_{18}H_{24}O_2N_2$, was first isolated by Grüning (Abstr., 1883, 369) from the rhizomes of *Nuphar luteum*, in the form of a colourless, sticky mass, which became syrupy at 65°. The authors have isolated the alkaloid from the same source by extraction with dilute hydrochloric acid, precipitation with silicotungstic acid, and decomposition of this precipitate with barium hydroxide. They found that the alkaloid when left in contact with barium hydroxide was slowly decomposed, yielding cinnamaldehyde, which was identified by the blood-red coloration which it produced with β-naphthol and sulphuric acid dissolved in alcohol (compare Deniges, *Bull. Soc. Pharm. Bordeaux*, 1908, 48, 267). T. A. H.

Morphine Series. I. Ethylthiocodides. Robert Pschorr and A. Rollett (*Annalen*, 1910, 373, 1—14).—The replacement of the bromine atom in bromocodide by hydroxyl, under suitable conditions, gives rise to three isomerides of codeine (compare Schryver and Lees, Trans., 1900, 77, 1024; 1901, 79, 563, 1408; Knorr and Hörlein, Abstr., 1907, i, 151, 956). Similarly, it is found that four isomeric ethylthiocodides may be obtained by replacing the bromine atom by the –SH group (compare Pschorr, Abstr., 1906, i, 877). The α-compound is formed by the action of ethyl mercaptan and aqueous sodium hydroxide on α-bromocodide at 100°; it is converted by an alcoholic solution of sodium ethoxide into the β-isomeride, which may also be prepared, therefore, by the action of an alcoholic solution of sodium ethoxide and ethyl mercaptan on α-bromocodide; a small quantity of a third γ-isomeride is formed in the latter case. The

δ-compound results from the action of ethyl mercaptan and sodium ethoxide on α-chlorocodide; β-chlorocodide gives rise to the same compounds as bromocodide.

An account of the chemical properties of β-ethylthiocodide, which differs in a marked degree from the other isomerides in reactivity, is given in a separate paper (compare following abstract). The α-, γ-, and δ-isomerides behave quite normally; they combine with methyl iodide, yielding methiodides, which are converted by aqueous alkalis into the corresponding ethylthiomethylmorphimethines. α-Ethylthiomethylmorphimethine, in analogy to the α- and γ-methylmorphimethines from codeine and *iso*codeine, is converted by sodium ethoxide into the β-isomeride, whilst the γ- and δ-ethylthiomethylmorphimethines, in analogy to the ε- and ζ-methylmorphimethines from ψ-codeine, are not altered by this reagent.

The degradation of the ethylthiomethylmorphimethines by Hofmann's reaction leads to the formation of known basic compounds and oily, nitrogen-free substances, except in the case of the δ-isomeride, which decomposes into trimethylamine and a crystalline vinyl compound.

α-Chlorocodide passes into β-chlorocodide when heated for a short time at 155—157° (compare Knorr and Hörlein, Abstr., 1908, i, 41); bromocodide does not undergo a similar rearrangement when heated.

α-Ethylthiocodide, $C_{20}H_{25}O_2NS$, crystallises in glistening rods, m. p. 88—89°, $[\alpha]_D^{20}$ −340° (in alcohol); the *hydriodide* forms glistening leaflets, m. p. 217° (corr.); the *methiodide*, $C_{20}H_{25}O_2NS,MeI$, decomposes at 236—237° (corr.), $[\alpha]_D^{20}$ −232·6° (in water). *α-Ethylthiomethylmorphimethine* is an oil; the *hydriodide*, $C_{21}H_{27}O_2NS,HI$, crystallises in glistening leaflets, decomposes at 204—206° (corr.), and has $[\alpha]_D^{20}$ −218·5° (in water); it may also be prepared by the action of ethyl mercaptan and aqueous sodium hydroxide on bromocodide methiodide; the *methiodide*, $C_{21}H_{27}O_2NS,MeI$, crystallises in slender needles, decomposes at 235—236° (corr.), and has $[\alpha]_D^{20}$ −183° (in water). The α-base is converted by *N*-sodium hydroxide solution into *β-ethylthiomethylmorphimethine*, $C_{21}H_{27}O_2NS$, which crystallises in yellow leaflets, m. p. 173—174° (corr.); the same compound is formed by the action of ethyl mercaptan and sodium ethoxide on bromocodide methiodide or chloromethylmorphimethine hydrochloride; the *methiodide* crystallises in needles and decomposes at 124—125° (corr.).

β-Ethylthiocodide has been mentioned previously (compare Pschorr, *loc. cit.*); it crystallises in prisms, m. p. 148°.

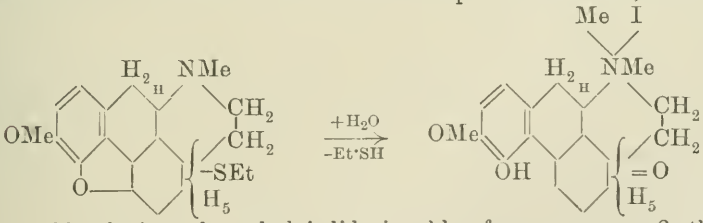
γ-Ethylthiocodide is an oil; the *methiodide* crystallises in small, glistening rods, and decomposes at 265—266°, $[\alpha]_D^{20}$ −119·2° (in water). *γ-Ethylthiomethylmorphimethine* is an oil; the *hydriodide* crystallises in leaflets, m. p. 179—180° (corr.), $[\alpha]_D^{20}$ −161° (in water).

δ-Ethylthiocodide is an oil, which slowly solidifies when kept; the *hydriodide* decomposes at 255° (corr.), $[\alpha]_D^{20}$ +51·4° (in water); the *methiodide* crystallises from water in prisms, decomposes at 230—234°, and has $[\alpha]_D^{20}$ +55° (in water); it also crystallises with 1Et·OH, and then has m. p. 143—145° (corr.). *δ-Ethylthiomethylmorphimethine* is an oil; the *hydriodide* crystallises in prisms, m. p. 196—197° (corr.), $[\alpha]_D^{20}$ +49° (in water); the *methiodide* forms small rods, m. p. 193—195° (corr.), $[\alpha]_D^{20}$ +39° (in water), and when boiled with *N*-sodium hydroxide solution yields trimethylamine and *ethylthiovinyltetrahydromorphenol*

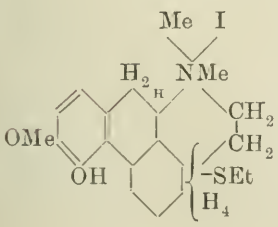
methyl ether, $C_{19}H_{20}O_2S$, which crystallises in prisms, m. p. 97—100°, $[\alpha]_D^{20}$ + 689° (in alcohol). W. H. G.

Morphine Series. II. β-Ethylthiocodide. Robert Pschorr (*Annalen*, 1910, **373**, 15—44. Compare preceding abstract).—β-Ethylthiocodide, when acted on by cold dilute hydrochloric acid for a short time, yields a sulphur-free compound, which is both phenolic and ketonic in character, and an ethyl mercaptan additive product of β-ethylthiocodide, thus: $2C_{18}H_{20}O_2N\cdot SEt + H_2O = C_{18}H_{21}O_3N + C_{18}H_{21}O_2N(SEt)_2$; an equivalent mixture of these two substances, when heated with hydrochloric acid, yields a substance containing sulphur, which is both phenolic and ketonic in character, and is also formed directly from β-ethylthiocodide by the action of hot hydrochloric acid: $C_{18}H_{21}O_3N + C_{18}H_{21}O_2N(SEt)_2 + H_2O = 2C_{18}H_{22}O_3N\cdot SEt$. The two ketones are readily converted one into the other; the sulphur-free ketone is extracted almost quantitatively by means of chloroform from an alkaline solution of the ketone containing sulphur, whilst an alkaline solution of the sulphur-free ketone in the presence of ethyl mercaptan, when treated with ammonium carbonate, yields the ketone containing sulphur. The transformation of β-ethylthiocodide into the ketone containing sulphur is accompanied by the migration of the ethylthiol group; this is demonstrated by the following series of changes: β-methylthiocodide, when warmed with hydrochloric acid, yields a ketone which contains the methylthiol group and combines with ethyl mercaptan, yielding a compound, $SMe\cdot C_{18}H_{21}O_2N\cdot SEt$; the latter substance, however, is not identical with the dimercaptyl compound formed from β-methylthiocodide, thus: $C_{18}H_{20}O_2N\cdot SMe + Et\cdot SH = SMe\cdot C_{18}H_{21}O_2N\cdot SEt$, but with that derived by similar means from β-ethylthiocodide and methyl mercaptan.

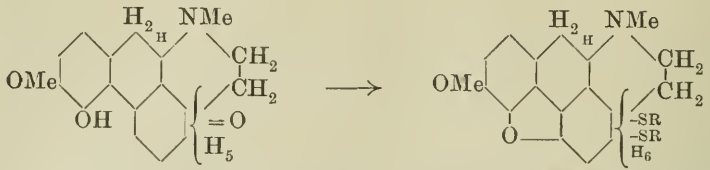
The action of an aqueous-alcoholic solution of methyl iodide on β-ethylthiocodide, in analogy to the action of hot hydrochloric acid, leads to the formation of the methiodide of the sulphur-free ketone, thus:



A cold solution of methyl iodide in chloroform converts β-ethylthiocodide into a compound having the annexed formula; when treated with acetic anhydride, it yields an acetyl derivative identical with the methiodide of the compound obtained by heating β-ethylthiocodide with acetic anhydride. The acetyl compound formed by the action of acetic anhydride on β-ethylthiocodide, when warmed with alkalis, is reconverted into β-ethylthiocodide; the regeneration of the oxygen-bridge which occurs in the



last case also takes place in the formation of the dimercaptyl compound by the action of mercaptan on the ketone, thus:



[With Krech.]—*β-Ethylthiocodide hydrochloride*, $C_{20}H_{25}O_2NS,HCl$, crystallises in prisms; when treated with cold *N*-hydrochloric acid solution for eighteen hours, it yields (1) *diethyldithiocodide*, the *methiodide* of which, $C_{22}H_{31}O_2NS_2,MeI$, forms glistening leaflets, m. p. 140—150°, and (2) a *ketone*, $C_{18}H_{21}O_3N$, which crystallises in prismatic plates, m. p. 145—147°, $[\alpha]_D^{20}$ −42·5° (in alcohol), and is also formed by boiling *β*-ethylthiocodide with hydrochloric acid; the *hydriodide*, $C_{18}H_{21}O_3N,HI,H_2O$, forms fan-shaped aggregates of small rods, melts at 165°, becomes solid subsequently, and decomposes finally at 265°; the *methiodide* crystallises in leaflets, decomposes at 251°, and yields an *acetate*, $C_{21}H_{26}O_4NI$, which crystallises in needles and decomposes at 269°; the *oxime*, $C_{18}H_{22}O_3N_2$, crystallises in leaflets, decomposes at 175—177°, and yields a *hydrochloride*, which forms needles decomposing at 282—283°; the *semicarbazone*, $C_{19}H_{24}O_3N_4$, crystallises in slender rods and decomposes at 247—248°.

The *ketone*, $C_{20}H_{27}O_3NS$, crystallises with $1H_2O$ in leaflets and small rods, m. p. 121—127°; the anhydrous substance has m. p. 182°; the *hydriodide* forms slender, matted needles and decomposes at 222—223° (corr.); the *methiodide* crystallises in glistening needles and decomposes at 241° (corr.); the *oxime*, $C_{20}H_{28}O_3N_2S$, forms tufts of small rods, m. p. 258° (corr.).

β-Ethylthiocodide interacts with methyl mercaptan in dilute hydrochloric acid, yielding a *substance*, $C_{21}H_{29}O_2NS_2$, which crystallises with 1Me·OH in small plates, m. p. 71—73°; the *methiodide* forms glistening leaflets, $[\alpha]_D^{20}$ +24·0° (in water), and decomposes at 146—147°.

β-Methylthiocodide, $C_{19}H_{23}O_2NS$, prepared from bromocodide and methyl mercaptan, crystallises in prisms, m. p. 124—125°, and interacts with ethyl mercaptan, yielding a *substance*, $C_{21}H_{29}O_2NS_2$, which crystallises in prisms, m. p. 112—115°, and forms a *methiodide*, leaflets decomposing at 184°, $[\alpha]_D^{20}$ +33·6° (in water); a *ketone*, $C_{19}H_{25}O_3NS$, is formed by heating *β*-methylthiocodide with dilute hydrochloric acid; it crystallises in prisms, m. p. 141—142°.

The *compound*, $C_{20}H_{25}O_2NS,MeI$, formed by the action of a cold solution of methyl iodide in chloroform on *β*-ethylthiocodide, crystallises in rectangular prisms and decomposes at 232°; the *acetate*, $C_{23}H_{30}O_3NIS$, crystallises in needles, m. p. 161°; the parent substance is converted by a strong aqueous solution of sodium hydroxide into the corresponding *betaine*, $C_{21}H_{27}O_2NS$, slender needles, m. p. 170—172°, which is converted by (1) a boiling alcoholic solution of methyl iodide into the *methiodide* of the *methyl ether*, $C_{22}H_{30}O_2NSI$, crystallising with 1Et·OH in leaflets, m. p. 209—211° (corr.); (2) an alcoholic solution of methyl iodide under pressure at 100° into a

substance, $C_{20}H_{26}O_3NI$, which contains two methoxy-groups and crystallises in plates, m. p. 260°; the betaine is converted by hot aqueous alkali into *β*-ethylthiomethylmorphimethine (compare preceding abstract).

ψ-Codeinone interacts with ethyl mercaptan in dilute hydrochloric acid yielding a *substance*, the *methiodide* of which, $C_{20}H_{25}O_3NS,MeI$, crystallises with 1Me·OH in leaflets, m. p. 204° (decomp., corr.), and is soluble in alkalis. W. H. G.

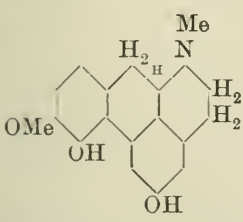
Morphine Series. III. Ethylthiomorphides. Robert Pschorr and Gerh. Hoppe (*Annalen*, 1910, 373, 45—50).—Bromomorphine reacts with ethyl mercaptan, yielding ethylthiomorphides analogous to the ethylthiocodides (compare preceding abstracts).

β-Ethylthiomorphide, $C_{19}H_{23}O_2NS$, is a crystalline substance, decomposes at 200—202°, and is converted (1) by cold dilute hydrochloric acid into *diethyldithiomorphide*, $C_{21}H_{29}O_2NS_2$, small prisms decomposing at 252°, and a *ketone*, $C_{17}H_{19}O_3N$, leaflets decomposing at 215—217°; (2) by 10% hydrochloric acid at a moderate temperature into a *ketone*, $C_{19}H_{25}O_3NS$, slender needles decomposing at 205—208°, the *hydrochloride* of the *oxime* of which, $C_{19}H_{26}O_3N_2S,HCl$, crystallises with $1H_2O$; and (3) by boiling with 10% hydrochloric acid into the ketone, $C_{17}H_{19}O_3N$, already described; the *oxime* of the latter substance decomposes at 260°, and yields a *hydrochloride*, $C_{17}H_{28}O_3N_2,HCl,H_2O$; the ketone is converted by acetic anhydride into a crystalline *diacetyl* derivative, the *methiodide* of which, $C_{21}H_{23}O_5N,MeI$, decomposes at 255—258°.

β-Ethylthiomorphide, when warmed with acetic anhydride and sodium acetate, yields an amorphous *diacetyl* compound, the *methiodide* of which, $C_{23}H_{27}O_4NS,MeI$, crystallises with 1Et·OH, in needles decomposing at 153°.

An *ethylthiomorphide*, crystallising in leaflets decomposing at 180°, was also obtained. W. H. G.

Morphine Series. IV. Constitution of Morphothebaine and Thebenine. Robert Pschorr (*Annalen*, 1910, 373, 51—74. Compare Pschorr and Massaciu, Abstr., 1904, i, 767; Knorr and Pschorr, Abstr., 1905, i, 814).—[With Hans Rettberg.]—1. *Morphothebaine.*—It is very probable that morphothebaine has the annexed



formula, since it closely resembles *apo*morphine in properties, and is formed from thebaine, presumably, without migration of the oxygen atoms. It has been found possible to obtain a tetramethoxyphenanthrene from morphothebaine, which, if the latter compound has the constitution given, must contain the methoxy-groups in the 1 : 3 : 5 : 6-positions; the synthesis of 1 : 3 : 5 : 6-tetramethoxyphenanthrene has been undertaken in order to decide this point.

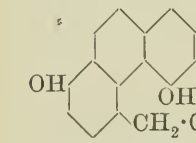
The silver salt of the trimethoxyphenanthrenecarboxylic acid derived from morphothebaine (compare Knorr and Pschorr, *loc. cit.*), when

heated at 250—280° under a pressure of 12 mm., yields a *trimethoxyphenanthrene*, the *picrate* of which, $C_{17}H_{16}O_3,C_6H_3O_7N_3$, has m. p. 104—120°. The *methyl* ester of the acid, $C_{19}H_{18}O_5$, crystallises in yellow, slender needles, m. p. 101—102°; the *ethyl* ester forms glistening leaflets, m. p. 83—84°; the *hydrazide*, $C_{18}H_{18}O_4N_2$, formed by the action of hydrazine hydrate on an alcoholic solution of the ester, crystallises in long, colourless needles, m. p. 176—177°, and is converted by amyl nitrite and an alcoholic solution of hydrogen chloride into the corresponding yellow *azoimide*, which, when heated with alcohol, passes into the corresponding *urethane* derivative, $C_{20}H_{21}O_5N$, long, pale pink needles, m. p. 137—138°. The latter substance is decomposed by a 10% alcoholic solution of ammonia at 150°, yielding *aminotrimethoxyphenanthrene*, the *hydrochloride* of which,

$$C_{17}H_{17}O_3N,HCl,$$

crystallises in long needles and decomposes at 250°; the amino-compound is converted through the diazo-derivative into the corresponding *hydroxy*-compound, which when methylated with methyl sulphate yields *tetramethoxyphenanthrene*, $C_{18}H_{18}O_4$, crystallising in flat, glistening needles, m. p. 108—109°; the *picrate* forms small, dark red needles, m. p. 147—148°.

[With Heinrich Loewen.]—II. *Thebenine.*—The annexed constitutional formula is assigned to thebenine for the following reasons:



(1) The trimethoxyphenanthrenecarboxylic acid, obtained by Pschorr and Massaciu from thebenine (*loc. cit.*), when heated yields 3 : 4 : 8-trimethoxyphenanthrene (compare Pschorr, Abstr., 1900, i, 233). (2) The methoxy-group must occupy position 3, since thebenine may be obtained from codeinone (compare Knorr and Hörlein, Abstr., 1907, i, 547), which contains a methoxy-group in position 3. (3) The $-C\cdot C\cdot N$ side-chain occupies position 5, since it readily undergoes ring-condensation with the hydroxyl group in position 4 with the formation of thebenol. It is definitely shown that the hydroxyl group in position 4 takes part in the formation of the new ring, since ethebenine also undergoes ring condensation, yielding ethebenol (compare Freund, Abstr., 1897, i, 495; 1899, i, 307), and the ethoxy-group in ethebenine is situated at 8, because it gives rise to 3 : 4-dimethoxy-8-ethoxyphenanthrene (compare following abstract).

Ethebenine is converted by sodium hydroxide and methyl sulphate into the *methosulphate* of *methethebenine*, $C_{24}H_{33}O_7NS$, which crystallises in slender needles, m. p. 241° (corr.); the corresponding *methiodide*, $C_{21}H_{27}O_3N,MeI$, has m. p. 252° (corr.). The methosulphate, when heated with alcoholic potassium hydroxide, yields 3 : 4-*dimethoxy*-8-*ethoxy*-5-*vinylphenanthrene*, $C_{20}H_{20}O_3$, which crystallises in yellow plates, m. p. 78°, and on oxidation yields 3 : 4-*dimethoxy*-8-*ethoxyphenanthrene*-5-*carboxylic acid*, $C_{19}H_{18}O_5$, crystallising in yellow needles, m. p. 191° (corr.); the latter substance, when heated at 195—205° under a pressure of 15 mm., yields 3 : 4-*dimethoxy*-8-*ethoxyphenanthrene*, $C_{18}H_{18}O_3$, leaflets, m. p. 100°, the *picrate* of which forms dark red needles, m. p. 119°. W. H. G.

Morphine Series. V. Synthesis of 3:4-Dimethoxy-8-ethoxyphenanthrene obtained by the Degradation of Thebenine. Robert Pschorr and F. Zeidler (*Annalen*, 1910, 373, 75—79).—An account of the synthesis of 3 : 4-dimethoxy-8-ethoxyphenanthrene, which is identical with the compound derived from ethebenine (compare preceding abstract).

o-Ethoxybenzyl chloride, $C_9H_{11}OCl$, is formed by the action of hydrogen chloride on *o*-ethoxybenzyl alcohol; it is an oil with an unpleasant odour, b. p. 125°/15 mm., and when boiled with potassium cyanide in acetone yields the *o-ethoxyphenylacetonitrile*, $C_{10}H_{11}ON$, a highly refractive liquid, b. p. 135—140°/16 mm.; the latter substance, when hydrolysed with alcoholic potassium hydroxide, yields *o-ethoxyphenylacetic acid*, $C_{10}H_{12}O_3$, a crystalline substance, m. p. 103°. The sodium salt of the latter substance, when heated with 2-nitro-3 : 4-dimethoxybenzaldehyde and acetic anhydride under pressure at 100° for ninety hours, yields *α-2′-ethoxyphenyl-2-nitro-3 : 4-dimethoxycinnamic acid*, $NO_2\cdot C_6H_2(OMe)_2\cdot CH{:}C(C_6H_4\cdot OEt)\cdot CO_2H$, which forms yellow crystals, m. p. 196°, and when reduced with ferrous sulphate and aqueous ammonia yields the corresponding *amino*-compound,

$$C_{19}H_{21}O_5N,$$

yellow prisms, m. p. 153°. The latter substance is converted through the diazo-derivative into 3 : 4-*dimethoxy*-8-*ethoxyphenanthrene*-9-*carboxylic acid*, $C_{19}H_{18}O_5$, which crystallises in glistening needles, m. p. 265°, and when heated with glacial acetic acid at 220° for eight hours yields 3 : 4-*dimethoxy*-8-*ethoxyphenanthrene*, $C_{18}H_{18}O_3$, which crystallises in leaflets, m. p. 100°, and forms a *picrate*, $C_{18}H_{18}O_3,C_6H_3O_7N_3$, red needles, m. p. 119°. W. H. G.

Morphine Series. VI. Transformation of Chloromethylmorphimethine into the Quaternary Salt of a Cyclic Base Derived from Phenanthrene. Robert Pschorr and F. Dickhäuser (*Annalen*, 1910, 373, 80—84).—A concentrated ethereal solution of chloromethylmorphimethine (compare Pschorr, Abstr., 1906, i, 877), when heated with alcohol at 100°, yields methylmorphol and probably chloroethyldimethylamine; instead of the latter compound, however, the polymeride, *N*-dimethylpiperazine dimethochloride, is obtained. On the other hand, chloromethylmorphimethine, when heated with benzene, yields an amorphous *substance*, which has the properties of a phenol and behaves as the salt of a quaternary base; the corresponding *methiodide* could not be obtained in a crystalline form, but when treated with aqueous sodium hydroxide and methyl sulphate, and subsequently with potassium iodide, yields a *methiodide*,

$$C_{19}H_{21}O_2N,MeI,$$

which contains two methoxy-groups, and crystallises with $1\frac{1}{2}H_2O$ in efflorescent, glistening needles. W. H. G.

Strychnos Alkaloids. VIII. Coloured Isomeric Salts of Cacothelin Base. Hermann Leuchs and Friedrich Leuchs (*Ber.*, 1910, 43, 1042—1051).—Bidemethylnitrobrucine hydrate (Moufang and Tafel, Abstr., 1899, i, 309) probably has the composition represented by the formula $C_{21}H_{21}O_7N_3$. It is shown that the base gives

rise to three groups of isomeric salts. The ordinary yellow salts, of which cacothelin is the nitrate, are transformed into isomeric green salts under the influence of sulphurous acid, and the green salts in their turn are transformed into violet salts. The function of the sulphurous acid appears to be purely catalytic, and the change can take place to a certain extent in the absence of the catalyst. Stannous chloride is a more efficient catalyst than sulphurous acid, and with this reagent it is difficult to isolate the intermediate green salts. Stannic chloride, zinc chloride, zinc and hydrochloric acid, and hydrogen sulphide do not act as catalysts.

Moufang and Tafel's nitrobrucine hydrate is shown to be identical with the base of cacothelin; it does not contain methoxy-groups.

A *sulphite*, $C_{21}H_{21}O_7N_3,H_2SO_3$, has been prepared by the action of sulphurous acid on the nitrate. It forms heavy, glistening, nearly colourless prisms.

The sulphate, $C_{21}H_{21}O_7N_3,H_2SO_4$, has been isolated in the yellow, green, and violet modifications. When the solution of the violet compound is kept, it changes to brown and ultimately to pale yellow, and the addition of dilute sulphuric acid to these two solutions yields the green and yellow salts respectively.

The violet *chloride*, $C_{21}H_{21}O_7N_3,HCl,2H_2O$, forms heavy, reddish-violet, rectangular prisms, and is the stable form. The yellowish-red chloride contains $1H_2O$, and forms minute, massive prisms or three- and six-sided plates, and decomposes at 250°. The green compound is unstable, and forms short prisms.

The nitrate has also been isolated in the three forms. J. J. S.

Syntheses with the Aid of Magnesium Pyrrole Compounds. II. Alkyl Pyrryl Ketones Bernardo Oddo (*Ber.*, 1910, **43**, 1012—1021. Compare Abstr., 1909, i, 672).—Acyl chlorides react readily with magnesium pyrryl iodide, yielding ketones of the type: $NH<^{C(CO\cdot R):CH}_{CH=\!-\!-=CH}$. In many cases the reaction is so violent that the addition of dry ether is necessary. The following have been synthesised by this method: 2-pyrryl methyl ketone and the corresponding ethyl, propyl, phenyl, and benzyl ketones. The yields are about 50—60% for the aliphatic, and about 80% for the aromatic, ketones. Several of these ketones have been prepared previously by Ciamician and Dennstedt (Abstr., 1885, 378), or by Dennstedt and Zimmermann (Abstr., 1887, 844), but the present method is preferable.

2-*Pyrryl propyl ketone*, $C_4NH_4\cdot CO\cdot C_3H_7$, forms colourless needles, m. p. 48·5°, b. p. 235—237°, and has an odour of butyric acid. The *phenylhydrazone*, $C_{14}H_{17}N_3$, forms pale straw-coloured needles, m. p. 80·5°. When oxidised with alkaline permanganate, the ketone yields the acid, $C_4NH_4\cdot CO\cdot CO_2H$ (compare Ciamician and Dennstedt, *loc. cit.*).

Neither oxime nor phenylhydrazone could be obtained from phenyl pyrryl ketone, which has b. p. 305—307°. Pyrryl ethyl ketone yields a *phenylhydrazone*, $C_{13}H_{15}N_3$, m. p. 111—112°, and benzyl pyrryl ketone, a *phenylhydrazone*, $C_{18}H_{17}N$, m. p. 133°.

The ketones react with magnesium methyl iodide in much the same manner as the original pyrrole. Indole also reacts with Grignard compounds. J. J. S.

Transformation of Oximinotriphenylpyrrole. Francesco Angelico and C. Labisi (*Gazzetta*, 1910, **40**, i, 417—423).—The ordinary methods of oxidation yield unsatisfactory results with oximinotriphenylpyrrole (compare Angeli and Angelico, Abstr., 1901, i, 45; Angelico and Calvello, Abstr., 1901, i, 747), which is, however, oxidised by means either of amyl nitrite in ethereal or alcoholic solution or of potassium permanganate in acetone solution, yielding the *compound*, $\begin{matrix}\mathrm{CPh{:}CPh}\\ \mathrm{N{=}{=}CPh}\end{matrix}\!\!>\!\mathrm{C{:}NO{\cdot}O{\cdot}NO{:}C}\!<\!\!\begin{matrix}\mathrm{CPh{:}CPh}\\ \mathrm{CPh{:}N}\end{matrix}$, as a red, crystalline powder, m. p. 190° (decomp.).

Reduction of this compound by means of zinc dust and acetic acid, hydroxylamine, ammonium sulphide, alcohol at a high temperature, or zinc dust and ammonium chloride yields the corresponding aminotriphenylpyrrole, whilst sodium arsenite or sulphide in alkaline solution gives oximinotriphenylpyrrole, which is probably a product intermediate between the new compound and aminotriphenylpyrrole. T. H. P.

New Trimethylenepyrrole Derivatives. I. Mario Ghiglieno (*Atti R. Accad. Sci. Torino*, 1910, **45**, 346—356).—The compound described by Guareschi and Grande (Abstr., 1900, i, 111) as 3 : 5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (dicyanohomocaronimide) is found to consist of a mixture of two apparently stereoisomeric compounds, the heterocyclic complex being, in the one case, on the side of the methyl group, and in the other, on the side of the ethyl group with respect to the trimethylene nucleus; this view is supported by the absence of such isomerism with the corresponding diethyl derivative.

α-3 : 5-Dicyano-4-methyl-4-ethyltrimethylenedicarbonimide,

$$\mathrm{NH}\!<\!\!\begin{matrix}\mathrm{CO{\cdot}C(CN)}\\ \mathrm{CO{\cdot}C(CN)}\end{matrix}\!\!>\!\mathrm{CMeEt},$$

forms colourless, rhombic crystals or prisms, m. p. 241—243° (decomp.) or 248—249° (Maquenne block). It has the normal molecular weight in boiling acetone, and has distinct acid properties, titration with sodium hydroxide in presence of phenolphthalein indicating it to be a monobasic acid. It is not attacked by bromine or alkaline permanganate, but by dilute sodium hydroxide (2 or 4 mols.) it is converted into the sodium salt of the monobasic acid,

$$\mathrm{NH}\!<\!\!\begin{matrix}\mathrm{CO{\cdot}C(CO_2H)}\\ \mathrm{CO{\cdot}C(CO{\cdot}NH_2)}\end{matrix}\!\!>\!\mathrm{CMeEt},$$

or of the dibasic acid, $\mathrm{NH}\!<\!\!\begin{matrix}\mathrm{CO{\cdot}C(CO_2H)}\\ \mathrm{CO{\cdot}C(CO_2H)}\end{matrix}\!\!>\!\mathrm{CMeEt}$, which are to be described later.

The *β*-isomeride, $C_{10}H_9O_2N_3$, forms colourless needles, m. p. 202—203°, and from ether separates in large crystals,

$$3C_{10}H_9O_2N_3,2Et_2O.$$

It is slightly more soluble than the α-form, has the normal molecular weight in boiling acetone, acts as a feeble, monobasic acid, and behaves towards dilute sodium hydroxide solution in the same way as the α-modification. T. H. P.

[Preparation of Aldehyde Condensation Products.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 218616).—A discusssion on the nature of the condensation products obtained from pyridinium chlorides with primary or secondary amines, and the preparation of dyes from these compounds (compare Zincke, Abstr., 1905, i, 241, 267, 923).

The aldehydes employed had the following general formula :

$$\begin{matrix}\mathrm{Alk}\\ \mathrm{Ar}\end{matrix}\!\!>\!\mathrm{N{\cdot}CH{:}CX{\cdot}CY{:}CZ{\cdot}C}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{H}\end{matrix},$$

where Ar = aryl, Alk = alkyl, X, Y, and Z = hydrogen or other substituted groups ; they were combined with dihydro-α-methylindole and various primary and secondary amines.

The *aldehyde*, NMePh·CH:CH·CH:CH·CHO, m. p. 79°, is described ; it forms an *oxime*, m. p. 127°, and a *phenylhydrazone*, m. p. 141°. The *aldehyde*, $\mathrm{CHO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}N}\!<\!\begin{matrix}\mathrm{C_6H_4{\cdot}CH_2}\\ \mathrm{CH_2{-}CH_2}\end{matrix}$, forms dark yellow prisms, m. p. 113°.

The *aldehyde*, $\mathrm{CHO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}N}\!<\!\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CHMe}\end{matrix}\!\!>\!\mathrm{CH_2}$, forms brownish-yellow leaflets, m. p. 126·5° ; its *oxime*, yellow needles, m. p. 181°.

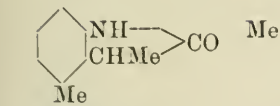
The *aldehyde*, $\mathrm{CHO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}N}\!<\!\begin{matrix}\mathrm{C_6H_4{-}O}\\ \mathrm{CHMe{\cdot}CH_2}\end{matrix}$, forms brown needles, m. p. 150°. F. M. G. M.

Preparation of Indoxyl and its Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 220172).—It is found that ethylenedianiline, $\mathrm{NHPh{\cdot}CH_2{\cdot}CH_2{\cdot}NHPh}$, its homologues, or derivatives when heated at 270—290° with alkali hydroxides and alkaline earth oxides are converted into indoxyls, from which indigotin derivatives are readily obtained. The preparations of indigotin from ethylenedianiline and of methylindoxyl from ethylenedi-*o*-toluidine are described in the patent. F. M. G. M.

Preparation of Indolinones from β-Acyl-*m*-tolylhydrazide. C. F. Boehringer and Söhne (D.R.-P. 218477 and 218727).—The formation of indolinones by heating β-acylphenylhydrazines with calcium oxide has previously been described ; the reaction with *o*- or *p*-tolylacylhydrazides is found to take place readily, whilst with *m*-tolylacylhydrazides isomeric indolinones are obtained, which are of great therapeutic value.

β-Propionyl-*m*-tolylhydrazide, m. p. 31°, prepared from propionyl chloride and *m*-tolylhydrazine, is heated at 200° with calcium oxide in the presence of an indifferent gas until the evolution of nitrogen ceases;

the two isomeric *indolinones* (annexed formulæ), m. p. 110° and 148—149°, are separated by extraction with benzene and subsequent crystallisation from methyl alcohol; they are sparingly soluble in water, readily so in mineral acids or alkalis, and reduce ammoniacal silver solutions. The second patent states that this reaction takes place at a lower temperature if sodium methoxide is employed.



F. M. G. M.

Derivatives of Tetrahydroquinoline. Franz Kunckell (*Ber. deut. Pharm. Ges.*, 1910, 20, 183—200).—A short account has been given already of some derivatives of tetrahydroquinoline, and in the present paper further compounds are described, which are likely to be of use in characterising this base (compare Abstr., 1905, i, 297).

6-Bromotetrahydroquinoline, prepared as described already (*loc. cit.*), yields a *hydrobromide*, m. p. 193—194°, a *sulphate*, m. p. 163°, *nitrate*, m. p. 199—200°, and a *platinichloride*, m. p. 204°, all of which are crystalline. On oxidation with permanganate, it furnishes pyridine-2:3-dicarboxylic acid, indicating that the bromine atom is in the benzene ring. On treatment with sodium nitrite, it gives a *nitrosoamine*, m. p. 89—90°, which crystallises in small, colourless needles, and on reduction is converted into the corresponding hydrazine, which condenses with benzaldehyde, yielding a crystalline product. Nitrous anhydride applied by Störmer's method (Abstr., 1899, i, 42) to 6-bromotetrahydroquinoline yields 6-*bromo*-8-*nitrotetrahydroquinolinenitrosoamine*, m. p. 120—121°, which crystallises in brick-red needles, gives Liebermann's reaction, and when heated with acetic acid passes into 6-*bromo*-8-*nitrotetrahydroquinoline*, m. p. 131—132°, crystallising in dark red plates and possessing no basic properties. This bromo-nitro base is reduced by stannous chloride to the corresponding *amino*-derivative, m. p. 85—86°, which crystallises in colourless needles, reduces platinic chloride solution, and gives an intensely red coloration with ferric chloride in presence of hydrochloric acid. The *hydrochloride*, m. p. 184°, crystallises in colourless leaflets, and forms with stannous chloride an *additive product*, $(C_9H_{11}N_2Br,HCl)_2SnCl_2,2H_2O$, m. p. 158—160° (decomp.), which forms rosettes of colourless needles, and is the form in which the amine is first isolated after reduction (see above).

When 6-bromotetrahydroquinoline, dissolved in alcohol at 30°, is treated with nitrous anhydride, 6 : 8-*dinitrotetrahydroquinoline*, m. p. 165—166°, is obtained; it crystallises from acetic acid or alcohol on addition of water, and is devoid of basic properties.

Acetyltetrahydroquinoline platinichloride, m. p. 146—147°, forms small, hard, reddish-brown crystals. On bromination the acetyl base yields either 6-bromoacetyltetrahydroquinoline hydrobromide (Abstr., 1905, i, 297) or *tribromotetrahydroquinoline hydrobromide*, depending on the conditions observed. The second of these has m. p. 252—253°, and forms a green, crystalline powder, which on addition of water

passes into a yellow *substance*, m. p. 169—171°, which crystallises from alcohol in small, colourless needles.

6-*Bromo*-8-*nitroacetyltetrahydroquinoline*, m. p. 155°, obtained by nitrating 6-bromoacetyltetrahydroquinoline, forms yellow leaflets, and is not basic. On reduction with stannous chloride, it yields a stannous chloride *additive product* with the hydrochloride of the corresponding amino-derivative, $(C_9H_{10}BrN_2Ac,HCl)_2SnCl_2$, m. p. over 270°, which crystallises in colourless or faintly yellow crusts. T. A. H.

Preparation of Mononitroanthraquinonylquinolines. Badische Anilin- & Soda-Fabrik (D.R.-P. 218476).—By the treatment of the three isomeric 1 : 2-, 2 : 1-, and 2 : 3-anthraquinonylquinolines with nitrating agents, compounds are formed which contain a nitro-group in the anthraquinone nucleus.

Nitroanthraquinonyl-1 : 2-*quinoline*, m. p. 248°, is a grey powder insoluble in water and alkalis, and soluble in mineral acids with yellow coloration.

Nitroanthraquinonyl-2 : 1-*quinoline*, yellow needles, m. p. 258°, is more readily soluble than the 1 : 2-isomeride.

Nitroanthraquinonyl-2 : 3-*quinoline*, yellowish-white crystals, m. p. 305°, is very sparingly soluble. F. M. G. M.

Naphthindole Bases. Josef Zangerle (*Monatsh.*, 1910, **31**, 123—134).—Phenylhydrazones of aldehydes and ketones containing the *iso*propyl group, when acted on by zinc chloride in alcoholic solution, lose ammonia and form indole bases (compare Brunner, Abstr., 1896, i, 169, 625; 1900, i, 360). This reaction is now extended to α- and β-naphthylhydrazones.

Methyl iso*propyl ketone-α-naphthylhydrazone* is a deep red, thick fluid oil. It is converted by alcoholic zinc chloride into 3 : 3 *dimethyl*-2-*methylene-α-naphthindoline*, $C_{10}H_6<^{NH\cdot C:CH_2}_{\quad\quad CMe_2}$, which crystallises from ether; m. p. 70—71°. The *picrate* forms dark yellow crystals, m. p. 149—150°; the *stannichloride* is reddish-yellow; the *mercurichloride* crystallises in colourless needles.

1 : 3 : 3-*Trimethyl*-2-*methylene-α-naphthindoline*, $C_{10}H_6<^{NMe\cdot C:CH_2}_{\quad\quad CMe_2}$, was obtained by decomposition of the *iodide* (m. p. 229°) with potassium hydroxide as a dark blue oil. The *picrate* forms light yellow crystals, m. p. 177°, and a crystalline *ferrichloride* and *platinichloride* were obtained.

1 : 1-Dimethyl-2-methylene-β-naphthindoline (or 3 : 3-dimethyl-2-methylene-ββ-naphthindoline) is best prepared by the action of alcoholic oxalic acid on the β-naphthylhydrazone of methyl *iso*propyl ketone. It has m. p. 115°, and is identical with the base described by Fischer and Steche (Abstr., 1887, 588). The iodide has m. p. 224—225°, the picrate also m. p. 224—225°, the acetate has m. p. 109°, and the benzoate forms colourless, flat crystals, m. p. 114°. Treatment with methyl iodide yields the tertiary base mixed with secondary base, which latter was removed as nitrosoamine, reddish-yellow crystals, m. p. 175—176°.

1 : 1 : 3-*Trimethyl*-2-*methylene*-β-*naphthindoline* (or 1 : 3 : 3-*trimethyl*-2-*methylene*-ββ-*naphthindoline*) has m. p. 119—120°; it turns blue on exposure to the atmosphere. The *iodide* crystallises in minute, colourless needles, m. p. 233°. E. F. A.

Preparation of Transformation Products of Ketens and Carbimides. Georg Schroeter (D.R.-P. 220852).—The greater part of the work described in this patent has been previously recorded (compare Abstr., 1909, i, 617, 773).

The following new compounds are mentioned: *Phenyltetrahydroxazolone*, m. p. 87—88·5°, obtained from phenylhydracrylic acid hydrazide. *Piperonyltetrahydroxazolone*, m. p. 122—123°, prepared from *piperonylhydracrylic acid hydrazide*, m. p. 173—174·5°. The methylation of piperonyltetrahydroxazolone yields *piperonylmethyltetrahydrooxazolone*, m. p. 108—109°, which on treatment with cold concentrated hydrochloric acid is converted into *methyleneadrenaline*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NHMe.$$

F. M. G. M.

Synthesis of Oxazoles and Thiazoles. II. Siegmund Gabriel (*Ber.*, 1910, **43**, 1283—1287).—It is shown that the reaction between compounds of the type of ω-benzoylaminoacetophenone and phosphorus pentachloride or pentasulphide (this vol., i, 190) is a fairly general one, and proceeds in the same manner when either or both the phenyl groups in ω-benzoylaminoacetophenone are replaced by aliphatic groups.

ω-*Acetylaminoacetophenone*, $NHAc{\cdot}CH_2{\cdot}COPh$, obtained by acetylating ω-aminoacetophenone hydrochloride with acetic anhydride and sodium acetate, crystallises in long, flat needles, m. p. 85·5—86·5°. The *hydrochloride* crystallises in flat, pointed needles, which lose hydrogen chloride on exposure to the air; the *platinichloride* crystallises in glistening rhombohedra, decomposing at 166°; the *aurichloride*, $2C_{10}H_{11}ON,HAuCl_4$, decomposes at 125°, and the *chromate*,

$$2C_{10}H_{11}ON,H_2CrO_4,$$

forms orange-red, rhombic plates, m. p. 83°, after sintering at 78°.

The crude acetyl derivative reacts with phosphorus pentachloride, yielding 5-*phenyl*-2-*methyloxazole*, $O<\begin{matrix}CMe{:}N\\ |\\ CPh{:}CH\end{matrix}$, which crystallises in glistening plates, m. p. 58—59°, b. p. 255·5°/748 mm. The oxazole yields a *chromate*, which crystallises in rhombic plates. 5-*Phenyl*-2-*methylthiazole*, $S<\begin{matrix}CMe{:}N\\ |\\ CPh{:}CH\end{matrix}$, obtained by heating the acetyl derivative with twice its weight of phosphorus pentasulphide for ten minutes at 170°, is pale yellow in colour, and has m. p. 81°. The *hydrochloride* crystallises in long needles; the *aurichloride* is precipitated as an oil which solidifies to yellow needles; the *platinichloride*, $2C_{10}H_9NS,H_2PtCl_6$, is sparingly soluble, and decomposes at 210°; the *chromate* forms orange-yellow needles, m. p. 108° (decomp.), and the *picrate*, flat prisms, m. p. 255—256°.

Benzoylaminoacetone, $COPh{\cdot}NH{\cdot}CH_2{\cdot}COMe$, obtained by benzoylating aminoacetone hydrochloride (Gabriel and Colman, Abstr., 1903,

i, 13), crystallises in needles, m. p. 85° (decomp.), and reacts with phosphorus pentachloride, yielding *2-phenyl-5-methyloxazole*,

$$O<\begin{matrix}CPh:N\\ |\\ CMe:CH\end{matrix}'$$

as an oil, b. p. 254—255°/734 mm. The *hydrochloride*, $C_{10}H_9ON,HCl$, forms glistening prisms and plates; the *aurichloride*, lemon-yellow needles; the *platinichloride*, striated prisms, which decompose at 218°, and the *chromate*, orange-yellow needles.

2-Phenyl-5-methylthiazole, $S<\begin{matrix}CPh:N\\ |\\ CMe:CH\end{matrix}'$, has b. p. 283·5°/750 mm., and has an odour of quinoline. The chromate and aurichloride are sparingly soluble, and the *platinichloride*, $2C_{10}H_9NS,H_2PtCl_6$, crystallises in yellow, rhombic plates, which decompose at 245°.

Crude acetylaminoacetone reacts with phosphorus pentachloride, yielding 2 : 5-*dimethyloxazole*, $O<\begin{matrix}CMe:N\\ |\\ CMe:CH\end{matrix}'$, with b. p. 117—118°/755 mm. It has an odour of pyridine, and yields a crystalline picrate, aurichloride, and platinichloride. The same acetyl derivative reacts with phosphorus pentasulphide, yielding 2 : 5-dimethylthiazole (Hubacher, Abstr., 1891, 222). J. J. S.

Mutual Replacement of Semicarbazone and Phenylhydrazone. Gustav Knöpfer (*Monatsh.*, 1910, **31**, 87—110. Compare Abstr., 1909, i, 188).—Phenylhydrazine and semicarbazide radicles mutually replace one another. The reaction is reversible and not complete; an equilibrium is reached, depending on the relative quantities of the interacting substances, which is not influenced by temperature. At least 5 mols. of the decomposing reagent are required to make the interchange practically complete. To test the relative strength of the attachment of the two groups, the action of aldehydes and ketones was studied towards a molecular mixture of phenylhydrazine and semicarbazide, but, as a rule, mixtures of both compounds were obtained, and no regularity could be detected. Differences in solubility also appear to have no great influence, although the semicarbazones are sparingly soluble and the hydrazones easily soluble.

Azines may be converted into hydrazones (Abstr., 1909, i, 188), but the reverse change could not be effected. The hydrazones of a large number of aldehydes and ketones were dissolved in alcohol, and set aside with three times the theoretical quantity of hydrazine sulphate and sodium carbonate. Only in the case of resorcylaldehyde was the azine formed.

The conversion of semicarbazone into hydrazone was effected in alcoholic or acetic acid solution; the reverse change was carried out by dissolving the phenylhydrazone in alcohol and adding semicarbazide, hydrochloride, and potassium acetate, dissolved in a minimum of water.

Derivatives of the following were investigated: benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, vanillin, anisaldehyde, cuminaldehyde, piperonal, furfuraldehyde, *o*-, *m*-, and *p*-nitrobenzaldehydes,

cinnamaldehyde, dimethylaminobenzaldehyde, resorcylaldehyde, protocatechualdehyde, acetophenone, *p*-aminoacetophenone, ω-bromo- and ω-chloro-acetophenones, and styryl methyl ketone.

Furfuraldehydesemicarbazone crystallises in brownish-yellow needles, m. p. 202—203°, but does not react with phenylhydrazine, nor does the reverse change take place. *Dimethylaminobenzaldehydesemicarbazone* forms colourless needles, decomp. 221—222°. *Resorcylaldehydesemicarbazone* separates in bright yellow crystals, which become red at 210°, decomp. 260°. *Protocatechualdehydesemicarbazone* is similar, and decomposes at 230°.

p-*Aminoacetophenonesemicarbazone* forms yellow crystals, m. p. 250° (decomp.); the *phenylhydrazone* forms faint yellow crystals, m. p. 110—114°; its *hydrochloride* is colourless (decomp. 215°), and not red, m. p. 207°, as described by Münchmeyer (Abstr., 1887, 482), and it does not react with semicarbazide. ω-*Bromoacetophenonesemicarbazone* separates in colourless crystals, m. p. 146°; only resinous substances were obtained from it on treatment with phenylhydrazine. ω-*Bromoacetophenonesemicarbazone* exhibits similar behaviour towards phenylhydrazine; it forms colourless, sparingly soluble crystals, m. p. 156°. Phenylhydrazine reacts with the ketone to form the same yellow halogen-free compound, m. p. 137°, as obtained by Hess (Abstr., 1886, 547) and Culmann (Abstr., 1890, 1268) from the bromo-compound.

E. F. A.

Synthesis with Diazomethane. New Preparation of Pyrazole. E. Oliveri-Mandalà (*Gazzetta*, 1910, 40, i, 117—120).—β-Methyl Δ^{β}-butylene and stilbene do not react with diazomethane, the substitution of several aliphatic or aromatic radicles for the ethylene hydrogen atoms apparently preventing the reaction.

The presence of one phenyl group, as in styrene, is also unfavourable to the reaction with diazomethane, which takes place slowly, giving 4-*phenylpyrazoline*, $NH<\begin{matrix}CH_2\cdot CHPh\\ |\\ N=\!=CH\end{matrix}$, which was analysed in the form of the *platinichloride*, $(C_9H_{10}N_2)_2,H_2PtCl_6$, and, on oxidation with bromine water, is converted into 4-phenylpyrazole (compare Buchner and Dessauer, Abstr., 1893, i, 282).

The interaction of vinyl bromide and diazomethane yields pyrazole hydrobromide; the unstable 5-bromopyrazoline, $NH<\begin{matrix}CHBr\cdot CH_2\\ |\\ N=\!=CH\end{matrix}$, is doubtless formed first, and is transformed into pyrazole by loss of hydrogen bromide, since Curtius and Wirsing (Abstr., 1895, i, 248) found that attempts to brominate pyrazoline always result in the formation of pyrazole. The readiness with which vinyl bromide and diazomethane react, confirms the view that the synthesis is favoured by the presence of a negative substituent group in the ethylene derivative.

T. H. P.

Preparation of Aqueous Soluble Compounds from 1-Phenyl-2:3-dimethyl-5-pyrazolones and Mono- or Di-alkylglycollic Acids of Formulæ $C_5H_{10}O_3$ and Upwards. J. D. Riedel (D.R.-P. 218478).—Soluble compounds from 1-phenyl-2:3-dimethyl-5-pyrazolone

(antipyrine) with alkylglycollic acids are readily prepared by melting together molecular proportions of the two components either with or without a diluent.

1-*Phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*isobutyrate, $OH\cdot CMe_2\cdot CO_2H, C_{11}H_{12}ON_2$,

colourless, prismatic needles, m. p. 71—72·5°, is prepared from dimethylglycollic acid (α-hydroxy*iso*butyric acid).

1-*Phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*-α-*ethylbutyrate*, m. p. 77·5—78·5°, crystallises from water.

1-*Phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*-α-*methylbutyrate*, $CMeEt(OH)\cdot CO_2H, C_{11}H_{12}ON_2$,

m. p. 64—65·5°, is prepared in ethereal solution.

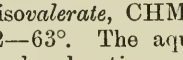
The hydrolysis of methyl *iso*propylketocyanohydrin, $CHMe_2\cdot CMe(OH)\cdot CN$,

yields α-hydroxy-αβ-dimethylbutyric acid, m. p. 72—72·5°, which combines with antipyrine to form 1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*-αβ-*dimethylbutyrate*, $CHMe_2\cdot CMe(OH)\cdot CO_2H, C_{11}H_{12}ON_2$, m. p. 78—79·5°.

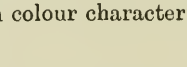
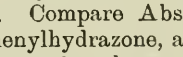
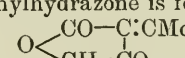
Antipyrine α-*hydroxy*isovalerate, $CHMe_2\cdot CH(OH)\cdot CO_2H, C_{11}H_{12}ON_2$, forms prisms, m. p. 62—63°. The aqueous solutions of these substances give a bluish-red coloration with ferric chloride, and with sodium nitrite the green colour characteristic of oximino-antipyrines.

F. M. G. M.

Derivatives of Acetyltetronic Acid. Erich Benary (*Ber.*, 1910, **43**, 1065—1069. Compare Abstr., 1909, i, 890).—α-Acetyltetronic acid forms a phenylhydrazone, an oxime, a semicarbazone, and a hydrazone. It is the carbonyl group of the acetyl group which reacts, as the same phenylhydrazone is formed when the amide,



reacts with an alcoholic solution of phenylhydrazine. The above-mentioned derivatives possess acidic properties.

α-*Acetyltetronic acid phenylhydrazone*,  , separates from methyl alcohol in rhombic crystals, m. p. 162—163° (decomp.), and when boiled with acetyl chloride and dry ether yields unaltered hydrazone, together with 1-*phenyl*-3-*methyl*-5-*hydroxymethylpyrazole*-4-*carboxylolactone*,  , which crystallises in colourless needles, m. p. 151—152°. The pyrazole derivative can also be obtained by boiling the hydrazone with amyl alcohol and phenylhydrazine hydrochloride. When boiled with methyl-alcoholic potassium hydroxide, the lactone yields 1-*phenyl*-3-*methyl*-5-*hydroxymethylpyrazole*-4-*carboxylic acid*,  , which crystallises in slender needles, decomposing at 212°. The potassium salt, when oxidised with permanganate, yields 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid.

When heated at 250°, the acid loses carbon dioxide, and yields

1-phenyl-3-methyl-5-hydroxymethylpyrazolone, $OH\cdot CH_2\cdot C\begin{matrix}NPh\cdot N\\ \|\\ CH-CMe\end{matrix}>CO$,

which crystallises in small plates, m. p. 116—117°.

α-Acetyltetronic acid semicarbazone, $C_7H_9O_4N_3$, crystallises in soft, felted needles, m. p. 212—213° (decomp.). The *oxime*, $C_6H_7O_4N,H_2O$, forms colourless needles, and when anhydrous melts at 149—150°.

The *hydrazone*, $C_6H_8O_3N_2$, forms colourless needles, m. p. 186—187°, and yields a *benzylidene* derivative, $C_{13}H_{12}O_3N_2$, m. p. 212—213°.

The *ketazine*, $C_{12}H_{12}O_6N_2$, crystallises in yellowish-green needles, which decompose at 225°. J. J. S.

Dehydracetic Acid. Erich Benary (*Ber.*, 1910, 43, 1070—1075. Compare Perkin, Trans., 1887, 51, 494; Stollé, Abstr., 1905, i, 838; Bülow, *ibid.*, 1909, i, 95).—Stollé's product, $\begin{matrix}O—CO—C-CMe\\ |\quad\quad\|\\ CMe:CH\cdot C\cdot NPh\end{matrix}>N$, melting at 158°, when boiled with alcoholic potassium hydroxide and acidified yields *1-phenyl-3-methyl-5-acetonylpyrazole-4-carboxylic acid*, $CH_2Ac\cdot C\begin{matrix}C(CO_2H)\cdot CMe\\ \|\\ NPh——N\end{matrix}$, which crystallises in small needles, m. p. 178—179°, and yields a sparingly soluble, crystalline *silver* salt, $C_{14}H_{13}O_3N_2Ag$. When heated for a short time at 220—230°, the acid loses water and yields the original compound, m. p. 158°. The *methyl* ester of the acid, $C_{15}H_{16}O_3N_2$, crystallises in colourless needles, m. p. 125°; the *oxime*, $C_{14}H_{15}O_3N_3$, has m. p. 209—211°. When oxidised, the acid yields 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid, m. p. 202—203° (Bülow and Schlesinger, Abstr., 1900, i, 56).

A much better yield (60%) of Stollé's lactone is formed when a methyl-alcoholic solution of dehydracetic acid is boiled with phenylhydrazine hydrochloride. It is accompanied by a *product*, $C_{13}H_{12}N_2$, m. p. 195—196°, which is not decomposed when boiled with alcoholic potassium hydroxide, and can be separated by this means from the lactone.

The behaviour of dehydracetic acid towards phenylhydrazine is analogous to that of acetyltartronic acid, and thus favours Feist's formula. J. J. S.

So-called Unsymmetric Methyl Azinsuccinate. August Darapsky (*Ber.*, 1910, 43, 1095—1111).—On heating ethyl diazosuccinamate with or without pyridine, a colourless, crystalline compound, m. p. 209°, is obtained, which gives a characteristic reaction with nitrous acid. It has the composition $C_{10}H_{12}O_5N_4$, and is derived from two molecules of the ester with elimination of a molecule of nitrogen and a molecule of alcohol.

This reaction is similar to the condensation of methyl diazosuccinate to *as*-methyl azinsuccinate (Curtius and Koch, Abstr., 1885, 886), m. p. 154°. This condensation product is now shown, however, to be identical with methyl 3 : 4 : 5-tricarboxypyrazolineacetate, obtained by Buchner and Witter (Abstr., 1894, i, 346) by the condensation of methyl aconitate and methyl diazoacetate.

Presumably, methyl diazosuccinate, $CO_2Me\cdot CH_2\cdot CN_2\cdot CO_2Me$, is

converted into methyl fumarate, $CO_2Me\cdot CH{:}CH\cdot CO_2Me$, which condenses with a second molecule of diazosuccinate to the pyrazoline, $NH<^{N=\!=\!=\!=\!=\!=\!=\!=\!=C\cdot CO_2Me}_{C(CO_2Me)(CH_2\cdot CO_2Me)\cdot CH\cdot CO_2Me}$. In confirmation of this, the condensation product is obtained in increased yield by the condensation of methyl fumarate and methyl diazosuccinate.

This synthesis proves the acetic acid residue to occupy position 5. By these operations, as Buchner and Witter (*loc. cit.*) found, a stereoisomeric ester, m. p. 104°, is obtained in small quantity.

In a similar manner, ethyl diazosuccinamate is, in part, converted into ethyl fumaramate, $CO_2Et\cdot CH{:}CH\cdot CO\cdot NH_2$, which condenses with ethyl diazosuccinamate to form an amic acid ester,

$$NH<^{C(CO\cdot NH_2)(CH_2\cdot CO_2Et)\cdot CH\cdot CO_2Et}_{\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-N{:}C\cdot CO\cdot NH_2}.$$

Alcohol is eliminated from this, forming *ethyl* 3 : 4 : 5-*tricarboxypyrazoline*-5-*acetate-amide-imide*,

$$\begin{matrix}CO\cdot CH_2\\ |\\ NH\cdot CO\end{matrix}>C<\begin{matrix}NH\!-\!-\!-\!-N\\ |\quad\quad\ |\\ CH(CO_2Et)\end{matrix}>C\cdot CO\cdot NH_2.$$

With nitrous acid the oximino-derivative is obtained. Proof of this structure is afforded by hydrolysis with sodium hydroxide to the corresponding acid, and methylation by means of diazomethane to the above-described methyl ester, m. p. 154°.

Ethyl diazosuccinamate is prepared by diazotising ethyl aspartate; attempts to obtain it by the action of ammonia on ethyl diazosuccinate led to a very violent explosion.

Ethyl 3 : 4 : 5-*tricarboxypyrazoline*-5-*acetate-amide-imide* forms colourless, intergrown, lustrous plates, m. p. 209° (decomp.), or when quickly heated, m. p. 215°. The *oximino*-derivative forms bright yellow, glistening plates, m. p. 198° (decomp.); it is soluble in alkali hydroxides with a yellowish-red coloration.

Methyl 3 : 4 : 5-tricarboxypyrazoline-5-acetate, obtained either from the above ethyl ester amide-imide or from methyl diazoacetate and trimethyl aconitate, or from dimethyl diazosuccinate and dimethyl fumarate, crystallises in colourless bunches of needles, m. p. 154°; at the same time a more soluble isomeride, m. p. 104°, is obtained, which is converted by hydrogen bromide in acetic acid into the higher melting ester. Nitrous acid is without action. E. F. A.

So-called Symmetrical Methylazinsuccinate. August Darapsky (*Ber.*, 1910, **43**, 1112—1126).—Both methyl and ethyl azinsuccinate were obtained as oils by Curtius (Abstr., 1885, 886) by coupling four molecules of diazoacetic ester. Buchner (Abstr., 1901, i, 232) suggested that in reality these oils represented impure esters of pyrazolinetricarboxylic acid. This supposition is now confirmed; the methylazin ester gives a series of liquid fractions of high boiling point containing nitrogen, and further purification of one of these yielded methyl *cyclo*propanetricarboxylate. The oil obtained on prolonged heating of ethyl diazoacetate at 120—130° gave, when kept, crystals of ethyl pyrazolinetricarboxylate. On distillation of the oil, *ethyl* trans-*cyclopropane*-1 : 2 : 3-*tricarboxylate*

was obtained, and identified by comparison with a synthetical product. It is a thick, colourless oil, b. p. 159—160°/9 mm.

Ethyl diazoacetate condenses both at 100° and at 120°; probably ethyl fumarate is first formed from two molecules. This condenses with a further molecule of ethyl diazoacetate to ethyl pyrazoline-3:4:5-tricarboxylate, $NH<\begin{matrix}N=\!\!=\!\!=C\cdot CO_2Et\\ CH(CO_2Et)\cdot CH\cdot CO_2Et\end{matrix}$. E. F. A.

4:6-Dimethyl-2-pyrimidone. III. Condensation with Aromatic Aldehydes. Otto Stark and Max Bögemann (*Ber.*, 1910, **43**, 1126—1131. Compare Abstr., 1909, i, 260).—The authors have condensed 4:6-dimethyl-2-pyrimidone with vanillin, protocatechualdehyde, and *p*-dimethylaminobenzaldehyde by the method previously described. In these cases only one methyl group reacts, so that only derivatives of the monobenzylidene type are obtained. With regard to the colour of the substances obtained from vanillin and protocatechualdehyde, the theory previously put forward holds good, but the dimethylaminobenzylidene derivative forms two series of differently-coloured salts. Phosphoric acid and all organic acids in all concentrations yield violet salts containing one molecule of acid. Very dilute (*N*/10) mineral acids (except nitric acid) also yield violet salts of the same type, but if the concentration of the acid exceeds *N*/3, yellow salts containing two molecules of acid are formed. Nitric acid yields yellow solutions at all concentrations. The yellow solutions become violet on dilution. It is suggested that the violet salts have the constitution:

$$NH<\begin{matrix}CO-NH\\ CMe:CH\end{matrix}>C:CH\cdot CH:C_6H_4:NMe_2Cl,$$

whilst to the yellow salts the formula

$$N<\begin{matrix}CO\cdot N(HCl)\\ CMe-CH_2\end{matrix}>C\cdot CH:CH\cdot C_6H_4\cdot NMe_2,HCl$$

is ascribed.

4-p-*Hydroxy*-m-*methoxybenzylidenemethyl*-6-*methyl*-2-*pyrimidone*, $C_{14}H_{14}O_3N_2$ (from vanillin), crystallises in yellow needles, m. p. 254°. The *hydrochloride* forms reddish-brown needles, m. p. 250° (sintering at 240°). The substance also yields a reddish-brown *acetate*, and a *sulphate* of the same colour, whilst the *nitrate* is yellowish-brown. The acetic acid solution dyes raw silk and cotton brown, but the colour is not fast to alkali.

4-m-p-*Dihydroxybenzylidenemethyl*-6-*methyl*-2-*pyrimidone*, $C_{13}H_{12}O_3N_2$ (from protocatechualdehyde), could not be obtained in good crystalline form. On heating to 300°, it loses colour, but does not melt. It dissolves in *N*/2-acids only on warming; in the case of nitric acid, this heating destroys the substance. The *sulphate*, *hydrochloride*, and *acetate* are brown. An acetic acid solution of the substance dyes raw silk, wool, and cotton brown, but the colour is not fast to alkali.

4-p-*Dimethylaminobenzylidenemethyl*-6-*methyl*-2-*pyrimidone*, $C_{15}H_{17}ON_3$,

crystallises in small, red laminæ, m. p. 250—252° (sintering at 245°). The *dihydrochloride* is prepared in alcoholic solution with hydrogen chloride in the absence of moisture, and crystallises in yellow needles. It rapidly turns violet in the air. The *monohydrochloride* is obtained by allowing the dihydrochloride to remain in a vacuum over potassium hydroxide. Acetic acid solutions of the substance dye silk, wool, and cotton violet, but the colour is not fast to alkali. R. V. S.

Preparation of Leuco-derivatives of Indigotins. Emanuel Merck and Wilhelm Flimm (D.R.-P. 217945).—When the products obtained by the condensation of grape or starch sugar with aromatic *o*-aminocarboxylic acids are fused with potassium hydroxide, and the dark or orange-red fusion subjected to atmospheric oxidation, derivatives of indigotin are obtained.

Glucoseanilide-o-carboxylic acid,

$$CO_2H\cdot C_6H_4\cdot N{:}CH\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH,$$

m. p. 126—128°, is prepared by heating an alcoholic solution of anthranilic acid with dextrose; on fusion with alkaline hydroxide, followed by oxidation, indigotin is produced. F. M. G. M.

Action of Primary Amines on Indigotin. Eugène Grandmougin (*Ber.*, 1910, 43, 1317—1318).—It is pointed out that the quindoline derivative obtained from aniline and indigotin (Abstr., 1909, i, 968) does not appear to be identical with Knecht's product (*J. Soc. Dyers*, 1898, 14, 163). J. J. S.

Preparation of Bromoindigotin Sulphide. Leopold Cassella & Co. (D.R.-P. 220321, 220629).—By the action of sulphur chloride (SCl_2) and sulphur bromide on indigotin at a temperature of about 160°, substituted indigotin sulphides are obtained.

Dibromoindigotin sulphide, $C_{16}H_6O_2N_2Br_2S$, is a blue powder, insoluble in most organic solvents, except nitrobenzene, and forms a valuable vat dye.

The second patent indicates that the preparation of brominated indigotin sulphides takes place readily when indigotin, bromine, and sulphur are heated together at a temperature above 160° in a diluting agent such as nitrobenzene or chlorobenzene.

Tribromoindigotin sulphide, prepared in this manner, is a dark blue, insoluble powder. F. M. G. M.

3-Aminotetrahydroquinazoline-2:4-dione or 3-Aminobenzoylenecarbamide. Franz Kunckell (*Ber.*, 1910, 43, 1021—1024. Compare Abstr., 1905, i, 382).—*3-Aminotetrahydroquinazoline-2:4-dione*, $C_6H_4<\begin{matrix}CO\text{—}N\cdot NH_2\\ |\\ NH\cdot CO\end{matrix}$, obtained by heating tetrahydroquinazoline-2:4-dione with hydrazine hydrate solution at 160—180° during twelve hours, crystallises in colourless needles, m. p. 290—291°. It sublimes readily, and reduces Fehling's solution and ammoniacal solutions of silver and platinum salts. When heated with concentrated hydrochloric acid at 160—170°, it is not decomposed, but when heated with 20% sodium hydroxide solution the amino-group is removed. The *hydrochloride*, $C_8H_7O_2N_3,HCl$, forms colourless needles, and decom-

poses at 289°. The *sulphate*, $2C_8H_7O_2N_3,H_2SO_4$, has m. p. 259—260°. The *acetyl* derivative, $C_6H_4<^{CO-N\cdot NHAc}_{NH\cdot CO}$, forms small, glistening needles, m. p. 250°, and the *di cetyl* derivative, $C_{12}H_{11}O_4N_3$, glistening needles, m. p. 212°.

3-*Methylaminotetrahydroquinazoline*-2 : 4-*dione*,

$$C_6H_4<^{CO-N\cdot NHMe}_{NH\cdot CO},$$

obtained by methylating the amino-compound, forms small needles, m. p. 263°. 3-*Benzylideneaminotetrahydroquinazoline*-2 : 4-*dione*,

$$C_6H_4<^{CO-N\cdot N:CHPh}_{NH\cdot CO},$$

has m. p. 240°. The *potassium* salt, $C_6H_4<^{CO-N\cdot NH_2}_{NK\cdot CO}$,EtOH, forms colourless prisms, and loses the alcohol of crystallisation at 180°.

J. J. S.

Constitution of 3-Aminotetrahydroquinazoline-2 : 4-dione and Some of its Derivatives. Franz Kunckell (*Ber.*, 1910, **43**, 1234—1238).—Proof is given in two ways that by the action of hydrazine hydrate on tetrahydroquinazoline-2 : 4-dione the imino-group in position 3 is replaced by the group $N:NH_2$ (compare preceding abstract).

In the first place, 1-methyltetrahydroquinazoline-2 : 4-dione was heated with hydrazine hydrate in a sealed tube at 160° to form 3-*amino*-1-*methyltetrahydroquinazoline*-2 : 4-*dione*,

$$C_6H_4<^{CO-N\cdot NH_2}_{NMe-CO}.$$

This crystallises in colourless needles, m. p. 165°, and is identical with the substance prepared by the action of methyl iodide on the potassium salt of 3-aminotetrahydroquinazolinedione.

The *benzylideneamino*-compound forms colourless needles, m. p 157°; the *o-hydroxybenzylideneamino*-derivative, prepared by interaction with salicylaldehyde, m. p. 160°, crystallises in lustrous, colourless plates; the *acetylamino*-derivative separates in colourless needles, m. p. 140°; the *methylamino*-derivative likewise crystallises in needles, m. p. 153°.

Secondly, 3-phenyltetrahydroquinazoline-2 : 4-dione,

$$C_6H_4<^{CO-NPh}_{NH-CO},$$

prepared by heating anthranilic acid and monophenylcarbamide at 180°, reacts with hydrazine, forming aniline and the 3-aminotetrahydroquinazoline-2 : 4-dione already described (*loc. cit.*). In addition, *o*-aminobenzhydrazide, m. p. 120—122°, and a substance crystallising in needles, m. p. 208—209°, are formed. E. F. A.

Combination of Triphenylmethane Dyes with the Indigotin Group. Fritz Reitzenstein and Wilhelm Breuning (*Annalen*, 1910, **372**, 257—286).—A continuation of the investigation on the effect of an accumulation of a large number of chromophoric groups on

the colour of a compound (compare Reitzenstein and Rothschild, Abstr., 1906, i, 316; Reitzenstein and Schwerdt, Abstr., 1907, i, 648). The compounds dealt with in this paper differ from those described in the previous communications in that the long carbon chain is replaced by the indigotin residue : $-NH>C:C<CO-NH-$.

Isatin, *o*-methylisatin, and *p*-methylisatin condense with tetramethyldiaminobenzhydrol under the influence of concentrated sulphuric acid, yielding the substances (I), (II), and (III) respectively $\left[R = -C_6H_4-NMe_2\right]$.

(I.) $CO<NH\cdot C:CH\cdot CH \atop CO--C:CH\cdot C\cdot CHR_2$ (II.) $CO<NH\cdot C:CMe\cdot CH \atop CO--C:CH-C\cdot CHR_2$

(III.) $CO<NH\cdot C:CH-CH \atop CO--C:C(CHR_2)\cdot CMe$ or $CO<NH\cdot C:CH\cdot C\cdot CHR \atop CO--C:CH\cdot CMe$.

These compounds are converted by phosphorus pentachloride into the corresponding substituted isatin chlorides, which, when treated with glacial acetic acid and zinc dust, yield the related di-indoxyl compound; for example, the substance (I) yields ditetramethyldiaminodiphenylmethyldi-indoxyl (IV).

The di-indoxyl derivatives, although leucoindigotin compounds, are not oxidised by atmospheric oxygen; indeed, the properties of the indigotin grouping are almost entirely obliterated by the presence of the triphenylmethyl complexes.

5-(4′ : 4″)-Tetramethyldiaminodiphenylmethylisatin (I) condenses with dimethylaniline in the presence of zinc chloride, yielding 5-(4′:4″)-tetramethyldiaminodiphenylmethyl-3 : 3-bis-*p*-dimethylaminophenyloxindole (V), which when oxidised by lead dioxide in acetic acid is converted into 4-amino-1 : 3-*bis*di-*p*-dimethylaminophenylmethylbenzene (VI) (compare Baeyer and Lazarus, Abstr., 1886, 155; Liebermann and Danaïla, Abstr., 1907, i, 976).

(IV.) $\left[CH--CH--C--NH>C- \atop C(CHR_2)\cdot CH:C\cdot C(OH)\right]_2$ (V.) $C_6H_3(CHR_2)--NH \atop C(C_6H_4\cdot NMe_2)_2\cdot CO$

(VI.) $CH<CH--C[CH(C_6H_4\cdot NMe_2)_2] \atop C(NH_2):C[CH(C_6H_4\cdot NMe_2)_2]>CH$.

A comparison of the dyes described in this paper shows that the colour depends largely on the absence or presence of methyl groups, and on their positions relatively to the fundamental carbon atom; compounds without a methyl group attached directly to the benzene nucleus are blue or bluish-violet, those with a methyl group in the ortho-position are green, whilst others with a methyl group in the meta-position are blue with a decided red tint. The colour is rendered more intense by the introduction of the $-NH\cdot CO\cdot CO-$ group with the $-NH-$ in the para-position, but not in the meta-position; in all cases, however, the colours are more brilliant and of a purer shade. Contrary to the general rule, the effect of increasing the size of the molecule, as in the case of the di-indoxyl derivatives, is not always to produce a change of colour towards violet.

5-(4′ : 4″)-*Tetramethyldiaminodiphenylmethylisatin* (I) is a yellowish-brown powder, and when oxidised by lead dioxide yields the corre-

sponding dye, which dyes wool a pure blue; the *acetyl* derivative, $C_{27}H_{27}O_3N_3$, is a bluish-white powder, and does not melt at 335°; the corresponding *chloride*, $CHR_2{\cdot}C_6H_3<^{CO}_{N}>CCl$, is a green powder, which when treated with glacial acetic acid and zinc dust yields *ditetramethyldiaminodiphenylmethyldi-indoxyl* (IV), a yellowish-brown powder which begins to decompose at 160°; the oxidised leuco-base dyes wool an intense deep blue.

5-(4′ : 4″)-*Tetramethyldiaminodiphenylmethyl*-7-*methylisatin* (II) is a yellowish-brown powder, m. p. 200—202°; after oxidation it dyes wool an intense blue with a reddish-tint. *Ditetramethyldiaminodiphenylmethyldi*-o-*methylindoxyl*, $C_{52}H_{56}O_2N_6$, is a bluish powder; it commences to decompose at 200° and sinters at 223°; when oxidised with lead dioxide, it dyes wool a brilliant violet.

4(or 6)-4′ : 4″-*Tetramethyldiaminodiphenylmethyl*-5-*methylisatin* (III) is a reddish-brown powder, m. p. 261°; the *sodium* salt is orange and has m. p. 222°. *Ditetramethyldiaminodiphenylmethyldi*-p-*methylindoxyl*, $C_{52}H_{56}O_2N_6$, is a green powder, which commences to decompose at 210° and sinters at 230°; the oxidised compound dyes wool a dark grass-green.

5-(4′ : 4″)-*Tetramethyldiaminodiphenylmethyl*-3 : 3-bis-p-*dimethylaminophenyloxindole* (V) is a yellowish-red, crystalline powder; it commences to decompose at 100°, and sinters at 120°. 4-*Amino*-1 : 3-bis*di*-p-*dimethylaminophenylmethylbenzene* (VI) is a white, crystalline powder, m. p. 149—150°; when oxidised with lead dioxide, it yields an intense blue solution with a faint red tint. W. H. G.

Syntheses with Diazomethane. II. E. Oliveri-Mandalà (*Gazzetta*, 1910, 40, i, 120—124).—Peratoner and Azzarello (Abstr., 1907, i, 979) and Peratoner and Palazzo (Abstr., 1907, i, 1018) found that the methyl or phenyl radicle in aceto- or benzo-nitrile hinders condensation with diazomethane, whilst the strongly negative halogen or cyanogen radicles have a favourable influence.

The author finds that condensation with diazomethane or diazoethane is facilitated by the carboxymethyl group of methyl cyanoformate. In this case the action proceeds in two stages:

(1) $CO_2Me{\cdot}CN + NH<^{CH}_{N} = NH<^{N:C{\cdot}CO_2Me}_{N:CH}$,

and (2) the latter $+ NH<^{CH}_{N} = NMe<^{N:C{\cdot}CO_2Me}_{N:CH}$. Both these products were isolated, the 2-methyl-1 : 2 : 3-triazole-4-carboxylic acid being identical with that obtained by Peratoner and Azzarello (*loc. cit.*) by hydrolysing 4-cyano-2-methyl-1 : 2 : 3-triazole.

The action of diazoethane on methyl cyanoformate yields the methyl ester of 4-*methyl*-2-*ethyl*-1 : 2 : 3-*triazole*-5-*carboxylic acid*, $NEt<^{N:C{\cdot}CO_2H}_{N:CMe}$; the free acid forms shining, feathery scales, m. p. 131°. T. H. P

Diazo-derivatives of [1 : 2 : 4-]Triazole. Wilhelm Manchot (*Ber.* 1910, 43, 1312—1317).—*Phenyldiazotriazole hydrate*, $C_8H_7ON_5$, obtained by treating phenylaminotriazole with an excess of nitrous acid, forms a yellow, crystalline precipitate, and, like the diazotriazolecarboxylic acid and its ester, is comparatively stable (compare Thiele and Manchot, Abstr., 1899, i, 168; Manchot and Noll, Abstr., 1906, i, 213). It is quite harmless when moist, but in the dry state explodes when heated, rubbed or struck, and liberates iodine from an acidified solution of potassium iodide. The compound can be used for the preparation of other derivatives of phenyltriazole; when the moist diazo-compound is added carefully to hydrobromic acid (D = 1·7°) at 0°, 5-*bromo*-3-*phenyl*-1 : 2 : 4-*triazole*, $CBr\begin{matrix}NH\cdot N\\ \| \\ N---CPh\end{matrix}$, is obtained as compact prisms, m. p. 186—188°, which can be reduced with water and sodium amalgam to 3-phenyltriazole, m. p. 116° (Young, Trans., 1905, 87, 626, gives 119—120°).

When reduced with stannous chloride and hydrochloric acid, the diazo-compound yields *phenyl*-1 : 2 : 4-*triazylhydrazine*, which forms a crystalline hydrochloride, $C_8H_9N_5,2HCl$, m. p. 198°, after sintering at 150°. The hydrazine reacts with aldehydes and ketones in alcoholic solutions, yielding hydrazones. The *benzylidene* derivative, $C_{15}H_{13}N_5$, forms prismatic crystals, m. p. 233°; the *anisylidene* compound, $C_{16}H_{15}ON_5$, has m. p. 195°; the o-*hydroxybenzylidene* derivative, $C_{15}H_{13}ON_5$, forms long needles, m. p. 269°, and the α-*phenylethylidene* derivative, $C_{16}H_{15}N_5$, long prisms, m. p. 255°.

Several condensation products of aminotriazoles and aldehydes have been prepared. *Piperonylideneamino*-3-*phenyl*-1 : 2 : 4-*triazole*, $C_{16}H_{20}O_2N_4$, forms slender needles, m. p. 194°, and *piperonylideneaminomethyltriazole*, $C_{11}H_{10}O_2N_4$, small prisms, m. p. 207°. J. J. S.

Action of Ammonia on ω-Nitrobenzaldehyde-*p*-nitrophenylhydrazone. Giacomo Ponzio (*Gazzetta*, 1910, 40, i, 77—86).—By the action of sodium methoxide, ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone is converted into α-dinitrotetraphenyltetrazoline (compare Bamberger and Grob, Abstr., 1901, i, 296), and a similar transformation is effected by the action of alcoholic potassium hydroxide (compare this vol., i, 192). With alcoholic ammonia, however, this compound yields (1) a small proportion of α-dinitrotetraphenyltetrazoline, and 2) a compound, $C_{13}H_{12}O_2N_4$, which is formed in 75—80% yield; the fact that this compound forms stable salts and gives a triazole when treated with acetic anhydride, together with the simultaneous formation of α-dinitrotetraphenyltetrazoline, indicates that the amino-group present occupies the position of the ω-nitro-group, so that it represents ω-aminobenzaldehyde-*p*-nitrophenylhydrazone (benzenyl-*p*-nitrophenylhydrazidine), $HN_2\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2$. This reaction, if of general application, affords a simple means of preparing substituted hydrazidines.

ω-*Aminobenzaldehyde*-p-*nitrophenylhydrazone*, $C_{13}H_{12}O_2N_4$, forms green prisms with a red reflexion, or reddish-brown needles with a

green reflexion, m. p. 150—151°, and has strongly basic properties, dissolving readily in all acids, and giving faintly yellow solutions; in alkali hydroxide solutions it dissolves, with formation of an intense wine-red coloration, but decomposes gradually with evolution of ammonia. Its *hydrochloride*, $C_{13}H_{12}O_2N_4,HCl$, forms yellow prisms, m. p. 245° (decomp.), and its *oxalate*, $C_{13}H_{12}O_2N_4,H_2C_2O_4$, faintly straw-yellow plates, m. p. 212° (decomp.).

3-*Phenyl*-1-p-*nitrophenyl*-5-*methyl*-1 : 2 : 4-*triazole*,

$$NO_2\cdot C_6H_4\cdot N\begin{matrix}N{=}{=}CPh\\ |\\ CMe{:}N\end{matrix},$$

prepared by the action of acetic anhydride on ω-aminobenzaldehyde-*p*-nitrophenylhydrazone, forms faintly yellow, rhombic plates, m. p. 142°. T. H. P.

New Method of Preparation of Hydrazidines. Giacomo Ponzio (*Gazzetta*, 1910, 40, i, 312—324).—By the method already described (see preceding abstract), the author has prepared a number of hydrazidines (amidrazones), which are all stable, intensely coloured compounds, forming hydrochlorides and, when they contain a *p*-nitro-substituent, oxalates. By the action of acetic anhydride they are converted into complex triazoles: $NH_2\cdot CR{:}N\cdot NH\cdot ArNO_2 \longrightarrow NHAc\cdot CR{:}N\cdot NH\cdot ArNO_2 \longrightarrow \begin{matrix}N{:}CMe\\ |\\ CR{=}N\end{matrix}\!\!>\!N\cdot ArNO_2$, which are not obtainable otherwise.

ω-*Nitrobenzaldehyde*-o-*nitrophenylhydrazone*,

$$NO_2\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

obtained in theoretical yield by the interaction of *o*-nitrobenzenediazonium sulphate and the sodium salt of ω-nitrotoluene, forms orange-red needles, m. p. 138—147°.

ω-*Aminobenzaldehyde*-o-*nitrophenylhydrazone*,

$$NH_2\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

prepared by the action of alcoholic ammonia on the preceding compound, forms brown prisms with green reflexion, m. p. 178°, and its *hydrochloride*, $C_{13}H_{12}O_2N_4,HCl$, shining, yellow plates, m. p. 258° (decomp.).

3-*Phenyl*-1-o-*nitrophenyl*-5-*methyl*-1 : 2 : 4-*triazole*,

$$NO_2\cdot C_6H_4\cdot N\begin{matrix}N{=}{=}CPh\\ |\\ CMe{:}N\end{matrix},$$

obtained by the action of acetic anhydride on ω-aminobenzaldehyde-*o*-nitrophenylhydrazone, forms faintly yellow needles, m. p. 143—144°.

ω-*Aminobenzaldehyde*-p-*nitro*-o-*tolylhydrazone*,

$$NH_2\cdot CPh{:}N\cdot NH\cdot C_6H_3Me\cdot NO_2,$$

obtained by the action of alcoholic ammonia on ω-nitrobenzaldehyde-*p*-nitro-*o*-tolylhydrazone (compare Abstr., 1909, i, 443; this vol., i, 192), crystallises in bronze-coloured plates with green reflexion, m. p. 119° (decomp.); its *hydrochloride*, $C_{14}H_{14}O_2N_4,HCl$, in yellow plates, m. p. 280° (decomp.), and its *oxalate*, $C_{14}H_{14}O_2N_4,H_2C_2O_4$, in yellow prisms, m. p. 232° (decomp.). With acetic anhydride, it yields 3-*phenyl*-1-p-*nitro*-o-*tolyl*-5-*methyl*-1 : 2 : 4-*triazole*,

$$NO_2\cdot C_6H_3Me\cdot C_2N_3PhMe,$$

which crystallises in straw-coloured, four-sided plates, m. p. 163—164°.

ω-Aminobenzaldehyde-o-nitro-p-tolylhydrazone, $NH_2 \cdot CPh{:}N \cdot NH \cdot C_6H_3Me \cdot NO_2$, prepared from the corresponding ω-nitro-derivative, forms slender, reddish-brown needles with green reflexion, m. p. 149°, and its *hydrochloride*, $C_{14}H_{14}O_2N_4,HCl$, yellow prisms, m. p. 260° (decomp.). Acetic anhydride, converts it into *3-phenyl-1-o-nitro-p-tolyl-5-methyl-1 : 2 : 4-triazole*, $NO_2 \cdot C_6H_3Me \cdot C_2N_3PhMe$, which crystallises in slightly yellow prisms, m. p. 120°.

ω-Aminobenzaldehyde-o-chloro-p-nitrophenylhydrazone, $NH_2 \cdot CPh{:}N \cdot NH \cdot C_6H_3Cl \cdot NO_2$, crystallises in orange-red or golden-yellow needles, m. p. 167—168°; its *hydrochloride* in flattened, straw-coloured needles, m. p. 278° (decomp.), and its *oxalate* in yellow laminæ, m. p. 245° (decomp.). By acetic anhydride, it is converted into *3-phenyl-1-o-chloro-p-nitrophenyl-5-methyl-1 : 2 : 4-triazole*, $NO_2 \cdot C_6H_3Cl \cdot C_2N_3PhMe$, which crystallises in slender, straw-coloured needles, m. p. 129°. T. H. P.

Reaction of Diazoalkyls with 1-Phenyl-2-methylurazole. Sidney Nirdlinger, E. K. Marshall, jun., and Salomon F. Acree (*Amer. Chem. J.*, 1910, **43**, 424—425).—A supplementary note to the previous paper (this vol., i, 341). Experiments are being made on the action of diazoalkyls on 1-phenyl-2-methylurazole at 0° and −70°. The ratios of the *N*- and *O*-esters obtained by the action of methyl iodide on the silver salt of 1-phenyl-2-methylurazole in 40% alcohol are the same whether the silver salt is suspended or dissolved. The ratios of the *N*- and *O*-esters obtained when the sodium, zinc, and silver salts of the urazole in alcohol-ether solution at −70° are treated with hydrochloric acid in presence of diazomethane are almost the same in each case, namely, 87 : 13. The urazole itself in alcohol-ether solution at 20°, 0°, or −70° gives a ratio 94 : 6, and hence it is evident that the salts have approximately the same equilibrium constants, and that these are slightly different from those for the urazole. The cause of this difference is being investigated. E. G.

Preparation of Substituted Halogen Iminodialkylpyrimidines. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 217946).—When iminodialkylpyrimidines are treated with halogenating agents, two atoms of halogen combine with the iminic nitrogen. *4-Dichloroamino 5 : 5-diethylpyrimidine-2 : 6-dione*, $\begin{matrix} NH \cdot CO \cdot C(Et)_2 \\ | \quad\quad | \\ CO\text{-}N{=}C \cdot NCl_2 \end{matrix}$, m. p. 147°, is thus prepared from 4-imino-5 : 5-diethylpyrimidine-2 : 6-dione. Prolonged boiling with water converts these substances into dialkylbarbituric acids. F. M. G. M.

Diazopyrroles. Francesco Angelico and C. Labisi (*Gazzetta*, 1910, **40**, i, 411—417).—It has been shown previously (Abstr., 1909, i, 122) that the cinnabar-red isomeride, into which diazotriphenylpyrrole is converted by prolonged boiling with dilute sulphuric acid, is oxidised by nitric acid to a diketone, the latter being transformed by zinc and acetic acid into the furan derivative corresponding with the diazo-

triphenylpyrrole. The authors now find that the reverse transformation of the furan derivative into diazotriphenylpyrrole can be effected by heating the former compound with alcoholic ammonia or ammonium acetate in a sealed tube.

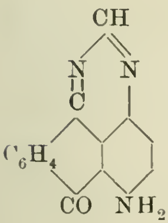
The action of alcoholic ammonium sulphide solution on the diketone, m. p. 163°, yields: (1) the *compound*, $\begin{array}{l} CH{:}CH{\cdot}C{\cdot}N{=\!=\!=}N \\ CH{:}CH{\cdot}C{\cdot}C(SPh){=}C{\cdot}SPh \end{array}$ (?), which forms yellow scales, m. p. 206—207° (slight decomp.), and yields a green substance on reduction with zinc dust and acetic acid; the fact that this green substance sublimes and gives a dark green solution with sulphuric acid indicates that it is probably formed by the elimination of one of the original sulphur atoms, the second of these taking part in the formation of a thiophen nucleus; (2) a small quantity of a faintly yellow *compound*, m. p. 196—197°.

The following salts of diazotriphenylpyrrole were prepared and analysed: the *sulphate*, $C_{22}H_{15}N_3,H_2SO_4$, greenish-yellow needles, m. p. 190° (decomp.); the *picrate*, $C_{22}H_{15}N_3,C_6H_3O_7N_3$, brown needles, m. p. 206° (decomp.), and the *nitrate*, $C_{22}H_{15}N_3,HNO_3$, m. p. 175° (decomp.), which is accompanied by a small proportion of an intensely yellow, crystalline compound, m. p. 183°.

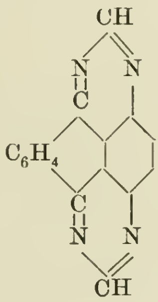
The action of magnesium ethyl iodide on diazotriphenylpyrrole yields an intensely yellow compound, $C_{24}H_{21}N_3$, m. p. 120°.

T. H. P.

Preparation of Anthrapyrimidines and of Anthrapyrimidones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 220314).—4-*Amino*-1-*anthrapyrimidine* (I) is formed by the condensation of 1 : 4-diaminoanthraquinone with one molecular proportion of formamide; with two molecules of formamide, *anthradipyrimidine* (II) is produced. 1-*Anthrapyrimidone*, yellow prisms, is prepared by heating together α-aminoanthraquinone, carbamide, and phenol.



(I.)



(II.)

The condensation of 4-amino-1-methylaminoanthraquinone with β-chloroanthraquinone yields 1-*methylamino*-4-β-*anthraquinonyl*-*aminoanthraquinone*, a dark blue powder, which when heated with carbamide, zinc chloride, and phenol forms 4-β-*anthraquinonylamino*-1-N-*methylanthrapyrimidone*.

4-p-*Tolylamino*-1-*anthrapyrimidone*, bronze prisms, is prepared from 1-amino-4-*p*-tolylaminoanthraquinone. The tinctorial properties of these compounds are described in the patent. F. M. G. M.

Chloroanthranilic Esters and their Condensation with Nitrosobenzene. PAUL FREUNDLER (*Compt. rend.*, 1910, 150, 1179—1181).—Directions are given for the preparation of *o*-carboxylic azo-compounds by direct chlorination of methyl anthranilate

and condensation of the product with nitrosobenzene (compare Abstr., 1906, i, 158). Condensation of methyl 5-chloroanthranilate with nitrosobenzene at the ordinary temperature gives, in addition to the *o*-azo-ester, azoxybenzene and a yellow *compound*,

$$C_{14}H_{11}O_3N_2Cl,$$

m. p. 137°. The reaction is represented as $3C_6H_5\cdot NO + C_8H_8O_2NCl = C_{14}H_{11}O_3N_2Cl + ON_2Ph_2 + H_2O$, and the constitution of the new compound as

$$CO_2Me\cdot C_6H_2Cl\langle\begin{matrix}NH\\O\end{matrix}\rangle NPh \text{ or } CO_2Me\cdot C_6H_2Cl\langle\begin{matrix}N\cdot NHPh\\|\\O\end{matrix}.$$

The substance is feebly basic, and forms blood-red, crystalline salts with mineral acids; the *acetyl* derivative crystallises in bronze-like needles, m. p. 124—125°. Hydrolysis with alkaline sodium hydroxide leads to the formation of a brownish-yellow *acid*, which, on reduction with zinc dust and subsequent oxidation in the air, furnishes a red *acid*. The latter forms a red *benzoyl* derivative, $C_{14}H_{10}O_3N_2ClBz$, m. p. 166°.

Analogous products were not obtained from methyl 3 : 5-dichloro- or 3 : 5-dibromo-anthranilate. W. O. W.

Diazohydrazo-compounds (Tetrazens). Diazo-compounds from Aminoguanidine. Karl A. Hofmann, Heinrich Hock, and Rudolf Roth (*Ber.*, 1910, **43**, 1087—1095. Compare this vol., i, 232).—The compound obtained by the action of sodium nitrite on aminoguanidine dinitrate, and previously described (this vol., i, 232) as aminoguanidine diazohydroxide, is more probably a pseudo-base, in which one nitrogen chain contains either the nitrosoamine group, ·NH·NH·NO, or the *anti*-diazohydroxide group, ·NH·N:N·OH, it being not possible at present to decide between these alternatives. The two carbon atoms are united by the diazohydrazo-group,

$$\cdot N{:}N\cdot NH\cdot NH,$$

and the compound is *guanylnitrosoaminoguanyltetrazen* or *guanyldiazoguanyltetrazen*, $NH{:}C(NH_2)\cdot NH\cdot NH\cdot N{:}N\cdot C(:NH)\cdot N_3H_2O$.

By the action of sodium hydroxide, cyanamide and ammonia are formed on the one hand, and, after acidifying, tetrazylazoimide on the other. This is analogous to the decomposition of hippurylphenylbuzylene studied by Curtius (Abstr., 1893, i, 463).

Guanyldiazoguanyltetrazen is stable towards ammonia, and neutral to litmus. It gives a reddish-yellow coloration with β-naphthol in alcoholic solution, and brownish-red and reddish-yellow colorations with α- and β-naphthylamine.

To exclude the possibility of the diazohydroxide containing a closed tetrazole ring, *guanyltetrazyltetrazen*,

$$NH{:}C(NH_2)\cdot NH\cdot NH\cdot N{:}N\cdot CN_4H,$$

was prepared by the interaction of diazotetrazole and aminoguanidine in acetic acid solution, and obtained as a bright yellow powder (compare Thiele, Abstr., 1892, 1295).

This is far less explosive than the diazohydroxide, is more soluble, and is acid towards litmus. It dissolves without colour in ethereal perchloric acid solution, and immediately reacts with silver nitrate, forming a yellow explosive silver salt. Decomposition by sodium

hydroxide likewise yields cyanamide, ammonia, and tetrazylazoimide.

When the diazohydroxide is decomposed by sodium hydroxide, the *compound*, $N_3 \cdot C(NH) \cdot N_3H_2O$, is probably formed, which is converted into tetrazylazoimide on acidifying. The addition of copper acetate to the alkaline solution gives a dark olive-brown precipitate, from which the *copper salt*, $N_3C\begin{matrix}\diagup N-Cu\cdot O\\ \diagdown NH\cdot N:N\end{matrix}$, was obtained in thin, bright blue plates; this is exceedingly explosive.

Guanylazoimide perchlorate, $NH:C(N_3) \cdot NH_2,HClO_4$, is obtained by the interaction of aminoguanidine dinitrate and sodium nitrite in presence of perchloric acid. It forms colourless, lustrous, doubly refractive, six-sided, thick plates. It is highly explosive, but otherwise resembles the analogous nitrate obtained by Thiele (Abstr., 1892, 1295). E. F. A.

The Quantity of Mono-amino-acids Yielded by Proteins when Hydrolysed with Acids. Thomas B. Osborne and D. Breese Jones (*Amer. J. Physiol.*, 1910, **26**, 212—228).—Modifications are proposed, and full details given of them, in the methods of esterifying organic acids on the lines of Phelps and Tillotson's work. The yield so obtained of most of the mono-amino-acids from protein (zein) is then greater. W. D. H.

Partial Hydrolysis of Proteins. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1910, **65**, 417—419).—The obtaining of *d*-alanylglycine from the partial hydrolysis of silk has been repeated, and in favourable cases as much as 8% is yielded. The mode of separation and identification of this dipeptide is described. W. D. H.

Partial Hydrolysis of Proteins by Sulphuric Acid Zdenko H. Skraup and E. Krause (*Monatsh.*, 1910, **31**, 143—148).—Proteins are dissolved by 60% sulphuric acid to a very different extent. Twenty grams were shaken at the ordinary temperature with 200 c.c. of acid (58·5%); gelatin, silk gum, and silk fibrin are dissolved almost immediately, casein requires somewhat longer, whilst egg-albumin and edestin are not completely dissolved after thirty-six hours.

From time to time, to test the extent of hydrolysis, samples were taken, diluted with water, made just alkaline with strong ammonia, and then faintly acid with sulphuric acid, and the amount of precipitation compared. Egg-albumin and edestin give a considerable proportion of albumoses, the silk proteins very little. In the latter case, hydrolysis takes place very rapidly, but the former substances are only slowly acted on. After three-quarters of an hour's interaction in the case of silk gum, the albumose precipitate only amounts to 29%. The albumoses from casein and edestin were dried, again dissolved in sulphuric acid, and precipitated after forty hours; a considerable proportion underwent further hydrolysis. E. F. A.

Production of Putrefaction Bases. Alexander Ellinger (*Zeitsch. physiol. Chem.*, 1910, **65**, 394—396).—A reply to Ackermann

(Abstr., 1909, i, 619, and this vol., i, 288). The author's previous results (Abstr., 1900, i, 143) are confirmed. J. J. S.

Preparation and Physico-chemical Properties of Demineralised Gelatin. Charles Dhéré and M. Gorgolewski (*Compt. rend.*, 1910, 150, 934—936).—Details are given for the preparation of ash-free gelatin by prolonged dialysis of aqueous solutions, conductivity water being employed in the last stages of the process. A more rapid method, applicable to small quantities of material, involves repeated freezing and filtration of 0·5% solutions. Whichever method is adopted, the last traces of electrolytes are removed by allowing a 2·25% solution to solidify in a U-tube, each limb of which is filled up with conductivity water; a current of 6 volts per cm. is then passed between platinum electrodes.

Gelatin prepared in this way was found to be electronegative, and to have a conductivity of $k = 5{\cdot}2 \times 10^{-6}$ in a 0·726% solution. Solutions have the power of spontaneous coagulation, although in a less degree than when electrolytes are present. A 2% solution shows a marked opalescence, which is diminished by alkalis and to a less extent by acids and salts. A 10% solution is not opalescent. W. O. W.

Pepsinglutinpeptone. Max Siegfried and H. Schmitz (*Zeitsch. physiol. Chem.*, 1910, 65, 295—317).—The authors have continued the examination of this substance, which was obtained by Scheermesser (Abstr., 1904, i, 463), with a view to ascertaining whether it had a constant composition and determining its decomposition products. They have found that different preparations of the compound have the same elementary composition (C 47·65%, H 6·69%, and N 17·30%). Different preparations of the barium salt had Ba 9·74—10·19%. The rotatory power was also practically constant, varying in different cases from $[\alpha]_D^{20} - 81{\cdot}28°$ to $- 82{\cdot}15°$. The substance when subjected to a fractional modification of the carbamino-reaction (Abstr., 1906, i, 144) yielded six fractions of barium salt, which had the same percentage of barium and the same rotatory power. Preparations of the peptone of different origins all showed the same value ($\frac{1}{7}$) for the quotient CO_2/N (compare Abstr., 1908, i, 379). β-Naphthalenesulphonyl chloride and 4-nitrotoluene-2-sulphonyl chloride yield *compounds* of constant composition, in which two of the acyl residues are present for every seven nitrogen atoms. The former has m. p. 205—210°; the latter, m. p. 165—170°. From all this the authors consider the chemical individuality and purity of the peptone to be established.

The hydrolysis of the substance was effected by means of sulphuric acid. Arginine and lysine were precipitated by addition of phosphotungstic acid, the amounts found being respectively 19·7% and 9·1%, on the assumption that no other compounds are contained in the precipitate. Glycine (49·2%), glutamic acid (9·3%), leucine, and proline were also found to be present. In the necessary separations the carbamino-reaction was largely employed. The percentages given above are the percentages of nitrogen contained in the various fractions expressed in terms of the total nitrogen of the peptone, but the amino-acids were actually isolated as well. R. V. S.

Pepsin. Serafino Dezani (*Atti R. Accad. Sci. Torino*, 1910, 45, 224—230).—The author has prepared an exceptionally active and pure specimen of pepsin, 0·00005 gram, dissolved in 50 c.c. of 0·25% hydrochloric acid solution, being capable of dissolving 1 gram of coagulated egg-albumin in eight hours. The pepsin contained 12·09% of nitrogen, 16·30% of which was basic nitrogen, existing as ammonia, 3·39%, histidine 4·46%, arginine 4·00%, and lysine 4·43%. Of the remaining 83·70% of nitrogen, 0·98% was insoluble, whilst 7·45% was precipitated by barium hydroxide, 13·44% by barium hydroxide, and magnesium oxide, 6·57% by silver sulphate, and 4·24% by phosphotungstic acid. There is hence a marked difference between pepsin and the proteins, since in the latter the proportions of nitrogen occurring in the form of the three hexone bases vary considerably, whilst in the case of pepsin these proportions are very nearly equal. Tyrosine, leucine, and, perhaps, aspartic and glutamic acids were also obtained on hydrolysis of the pepsin. T. H. P.

Proteolytic Ferments. K. Hirayama (*Zeitsch. physiol. Chem.*, 1910, 65, 290—292).—From experiments on the action of commercial preparations of pepsin and of the gastric juice of the dog, the author has obtained results confirming the indications of Takemura (*ibid.*, 63, 201) that these products contain another ferment of the type of β-protease. The method adopted was to act on egg-albumin with Grübler or Merck pepsin, or with the gastric juice in the presence of small quantities of acids of different strengths. The rate of solution of the protein (measured by Mett's method) and the rate of production of carboxyl groups (measured by Sörensen's formaldehyde titration) are differently affected by the change in the degree of acidity of the medium, indicating that two distinct fermentative processes are involved. R. V. S.

Influence of Reaction of the Medium on the Formation of Melanins by Diastatic Oxidation. H. Agulhon (*Compt. rend.*, 1910, 150, 1066—1068. Compare Abstr., 1909, i, 621).—Strong acids diminish the yield of melanins obtained by the oxidation of tyrosine with an extract of *Russula queleti*, whilst boric acid and salts, such as monosodium phosphate, which are neutral to methyl-orange are without action. Salts neutral to phenolphthalein and alkaline to methyl-orange favour the formation of insoluble oxidation products, the optimum concentration being between $N/200$ and $N/100$. Sodium hydroxide and salts, such as disodium phosphate, which are alkaline to phenolphthalein favour oxidation up to an optimum concentration of $N/500$, above which they have an inhibiting effect. W. O. W.

The Influence of Neutral Salts on Ferment Action. Emil Starkenstein (*Biochem. Zeitsch.*, 1910, 24, 210—218).—The diastatic enzyme loses its power after dialysis. This power can, however, be restored on the addition of sodium chloride. A certain definite quantity of salt is necessary to produce the optimum action; excess above this quantity causes inhibition; the absolute and not the relative quantity is the factor determining this optimum. If a diastase solution, inactivated by dialysis, is shaken with insoluble starch, it is adsorbed. On addition of salt to a suspension of the

starch with the adsorbed ferment, the latter is reactivated. The author draws the conclusion that the adsorption is a physical and not a chemical process, as he shows that the ferment is adsorbed from a solution containing soluble starch by insoluble starch. S. B. S.

Viscosaccharase, an Enzyme which Produces Slime from Cane-Sugar. Martinus W. Beyerinck (*Proc. K. Akad. Wetensch., Amsterdam*, 1910, 12, 635—649).—Certain bacteria, such as *B. mesentericus vulgatus* and *B. megatherium*, when grown on a medium of the composition: tap-water, 2% agar, 2% saccharose, 0·02% potassium nitrate, 0·02% dipotassium hydrogen phosphate, produce an emulsion. This phenomenon is due to an enzyme, *viscosaccharase*, which diffuses out into the agar-plate, and which can be precipitated (along with other enzymes) from filtered cultures of *B. mesentericus*. A reducing sugar is formed at the same time as the colloidal substance, to the formation of which the emulsion is due. The viscosaccharase appears to be an enzyme capable of producing synthesis, and a relationship is supposed to exist between the synthetically produced colloid and "dextran." Saccharose may be replaced by raffinose, but other sugars investigated do not give rise to the emulsion. S. B. S.

Enzymic Condensation of Sugars. Enrico Pantanelli and G. Faure (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 389—394).—When *Aspergillus oryzae* is grown on a solid or liquid nutrient medium containing starch, its amylolytic activity increases, even after the formation of spores, and passes through a maximum after thirty to forty days at 25°. An enzyme which has the power of condensing dextrose or invert sugar first appears after thirty-five to forty days, when the amylolytic activity has begun to decline, and increases in amount slowly, but irregularly, until the eighth month, subsequently disappearing. Amylase, maltase, and invertase are found in small quantities in year-old cultures. The activity of the condensing enzyme excreted in the culture liquid is considerably less than that of the enzyme contained in the mycelium, and the authors have investigated the action of 5 c.c. of mycelium extract (1 : 5), in presence of toluene, on 15 c.c. of (1) concentrated solutions of dextrose and invert sugar (about 4 mols.) and sucrose (about 2 mols.), and (2) saturated lactose solution at 45° and at the ordinary temperature.

In a control solution of dextrose, the amount of reducing sugar per 1 c.c. diminished in one hundred and fifteen days from 0·736 to 0·528 gram, the latter figure being obtained in presence of the enzyme in four to eleven days. Cryoscopic measurements indicate, in the concentrated dextrose solutions containing enzyme, a diminution of the molecular concentration (4·09 to 3·24 mols. at 45°), so that a proportion of the original hexose molecules have undergone condensation to larger molecules possessing little or no reducing power. In the control solution of dextrose, the molecular concentration diminishes, under similar conditions, from 4·09 to 3·49, so that, in absence of enzyme, a reducing polysaccharide, probably maltose or *iso*maltose, is formed. In invert-sugar solutions, the enzyme causes loss of reducing power without effecting condensation of the sugar molecules, the reversion being hence only apparent.

Reversion of a hydrolytic change only occurs when the concentration of the products of hydrolysis exceeds that which represents equilibrium with the hydrolyst. In highly concentrated solution, the hydrolytic reaction must be regarded as bimolecular, the small proportion of water assuming the role of an active mass, and not that of a mere solvent. When, however, 2 of the 4 mols. of dextrose were replaced by 2 mols. of a neutral salt, no condensation was effected by the enzyme, the reversionary activity of which may be paralysed by the salt or its ions. If, instead of 2 mols. of neutral salt, 2 mols of mannitol were employed, condensation occurred to the extent of 36·2% at the ordinary temperature, so that either the mannitol condenses with the dextrose, or the assumption that the water figures as an active mass in the reaction is justified.

In neutral solution, the mycelium of *Aspergillus oryzae*, or its aqueous or glycerol extract, causes no condensation of maltose, but in presence of a small proportion of sodium hydroxide, condensation occurs in a syrup containing 68—70%, or even in a solution containing only 8—10% of the sugar; the synthesising enzyme which effects this condensation of maltose differs from the amylase (or dextrinase), which, in an acid medium, hydrolyses starch (or dextrin) to maltose. T. H. P.

Action of Hypophosphorous Acid on Triphenylcarbinol and on Michler's Hydrol. II. Robert Fosse (*Bull. Soc. chim.*, 1910, [iv], 7, 231—235. Compare this vol., i, 292).—When triphenylcarbinol is heated with hypophosphorous acid and the yellow product boiled with sodium hydroxide solution, an oily residue is formed, consisting of triphenylmethane with a little triphenylcarbinol; the solution yields crystals of *triphenylmethylphosphinous acid*,

$$CPh_3\cdot PHO\cdot OH,$$

m. p. 94°. When the reaction is carried out with sodium hypophosphite in presence of acetic acid and sulphuric acid, the carbinol is almost completely converted into the acid, whilst in presence of acetic acid alone, an almost quantitative yield of the hydrocarbon is obtained.

Tetramethyldiaminobenzhydrylphosphinous acid,

$$CH(C_6H_4\cdot NMe_2)_2\cdot PHO\cdot OH,$$

prepared from Michler's hydrol, occurs in colourless crystals, m. p. 90°. This acid reduces an alcoholic solution of silver nitrate on boiling. W. O. W.

Reduction Products of Arsanilic Acid and its Derivatives. I. *p*-Aminophenylarsinic Oxide. Paul Ehrlich and Alfred Bertheim [and, in part, E. Schmitz] (*Ber.*, 1910, 43, 917—927).—Arsanilic acid may be reduced to *p*-aminophenylarsenic oxide (1) with sulphurous acid in presence of hydrogen iodide as catalyst, or (2) with phenylhydrazine, or (3) with phosphorus trichloride, in an indifferent diluent, such as ethyl acetate. The last method is the least satisfactory in the particular case studied.

p-minophenylarsenic oxide, $NH_2\cdot C_6H_4\cdot AsO,2H_2O$, softens at 80°, becomes liquid, and decomposes at 100°. The anhydrous substance softens at 90°, partly melts at 100°, becomes solid, and melts to a

clear and transparent liquid at 185—186°. It has only very faint acid properties, but is a strong reducing agent. It forms azo-dyes of yellow colour with a distinct red tinge, and a red *condensation product* with β-naphthaquinonesulphonic acid, very sparingly soluble in sodium carbonate.

In the amino-compound the bond between arsenic and carbon is much looser than in arsanilic acid; in addition, it behaves as an unsaturated compound, the arsenic tending to react as a quinquevalent atom. Accordingly, it is very reactive.

Hydrogen chloride converts it into *triaminotriphenylarsine*,

$$As(C_6H_4\cdot NH_2)_3;$$

this forms glistening, four-cornered plates, m. p. 173—174°; the *triacetate* crystallises in colourless needles, which soften at 170°, m. p. 232—233°. Iodine oxidises it to *triacetaminotriphenylarsenic oxide*, $AsO(C_6H_4\cdot NHAc)_3$.

p-Aminophenylarsenic oxide reacts with chloroacetic acid, forming p-*aminophenylarsinoacetic acid*, $NH_2\cdot C_6H_4\cdot AsO(OH)\cdot CH_2\cdot CO_2H$, crystallising in plates, m. p. 162° (decomp.).

The halogen alkyls react similarly. E. F. A.

Preparation of Arsenoaryl-glycollic and -thioglycollic Acids. [Arsenoaryl-oxy- or -thio-acetic Acids.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 216270. Compare Abstr., 1909, i, 279, 280, 348).—The reduction of hydroxyarylarsinic acids has been described previously, but it is now found that with such strong reducing agents as sodium amalgam or sodium hyposulphite, products of the following general formula are produced:

$$2CO_2H\cdot CH_2\cdot R\cdot A\cdot AsO(OH)_2 + 8H = CO_2H\cdot CH_2\cdot R\cdot A\cdot As{:}As\cdot A\cdot R\cdot CH_2\cdot CO_2H,$$

A = aryl; R = oxygen or sulphur.

Phenylglycol-p-*arsinic acid*, prepared by heating sodium *p*-hydroxyphenylarsinate in aqueous alkaline solution with chloroacetic acid, crystallises from water, sinters about 150°, and carbonises on further heating.

Phenylthioglycol-p-*arsinic acid*, readily soluble in hot alcohol, is produced when diazotised *p*-aminophenylarsinic acid is boiled with potassium xanthate in alkaline solution and subsequently treated with chloroacetic acid; it sinters at 170°, and decomposes about 187°.

Arsenomandelic acid, $As_2(C_6H_4\cdot O\cdot CH_2\cdot CO_2H)_2$, is obtained when sodium phenylglycol-*p*-arsinate is reduced in alkaline solution at 45° with sodium hyposulphite and magnesium chloride; the *sodium* salt is yellow, and readily soluble in water, from which the free acid separates as a voluminous precipitate on acidification; it reduces cold ammoniacal silver nitrate.

Arsenophenylthiolacetic acid has similar properties; it is prepared by heating phenylthioglycol-*p*-arsinic acid with phenylhydrazine in methyl alcoholic solution, when *arsenoxidephenylthiolacetic acid* is formed; sodium amalgam is then added, when *sodium arsenophenylthiolacetate* separates as a yellow precipitate.

These compounds have powerful trypanocidal properties.

F. M. G. M.

Organic Chemistry.

Theory of the Formation of Ethylene. Robert Kremann (*Monatsh.*, 1910, 31, 211—220).—Experiments have been made on the reaction between ethylene and sulphuric acid by heating the two together in the proportions 1 : 4 gram-mols. The experiments were conducted in a sealed bulb attached to a manometer, and the mercury adjusted so that the volume was kept constant. At all temperatures up to 110°, slow absorption took place until equilibrium had been established (at 57° $p = 115$, at 99° $p = 240$, and at 107° $p = 270$ mm.). Above 111° absorption took place for a short time, but was followed by a rapid increase of pressure due to secondary reactions, for example, the formation of carbon monoxide and sulphur dioxide. Even at the higher temperatures, it was found possible to minimise the effects of the secondary reactions by allowing the mixture to remain at a lower temperature until a pressure was obtained which was close to that corresponding with the higher temperature, and then to plunge the vessel into the bath at the higher temperature. If the pressure was correct, no diminution occurred, but after some time there was a rapid increase of pressure due to the secondary reactions. The value of Q (the algebraic sum of the heat of formation of 1 gram-mol. of ethyl hydrogen sulphate from the alcohol and acid and the heat of solution of this sulphate in the liquid phase) has been calculated from the equation $\log p_1/T_1 - \log p_2/T_2 = Q/R.T_2 - T_1/T_1T_2$, and has a value of about − 3·4 Cal.

Similar experiments have been made by heating ethyl hydrogen sulphate (1 mol.) with sulphuric acid (3 mols.), but experimental difficulties were experienced owing to the secondary reactions. At 99° the pressure rose rapidly at the beginning, then more slowly, remained constant for a short time, and again increased, probably owing to the secondary reactions which are facilitated by the catalytic influence of the carbon formed during the reaction.

The results agree with the view that alcohol and sulphuric acid react instantaneously, forming water and ethyl hydrogen sulphate, and that the latter then decomposes into ethylene and sulphuric acid.

J. J. S.

Preparation of Organic Iodides from the Corresponding Bromides and Chlorides. Hans Finkelstein (*Ber.*, 1910, 43, 1528—1532. Compare Perkin and Duppa, *Annalen*, 1859, 112, 125; von Romburgh, Abstr., 1883, 303).—One of the best methods of replacing the chlorine or bromine of an organic compound by iodine is to treat with an acetone solution of sodium iodide. In many cases the reaction is instantaneous, and in all cases where reaction proceeds, a precipitate of sodium chloride or bromide is formed.

The relative reactivities of halogen derivatives towards sodium iodide do not appear to be the same as their reactivities towards

water or methyl alcohol; thus primary alkyl bromides react most readily with sodium iodide, and the tertiary least readily.

The method does not work with acyl chlorides or with chloro- or bromo-compounds, which yield unstable iodo-derivatives. This is usually the case with compounds containing several carbonyl, carboxyl, or phenyl groups; in such cases one of the following changes occurs: (1) Formation of an ethylene linking, for example, $\alpha\beta$-dibromo-β-phenylpropionic acid yields cinnamic acid; (2) ring formation, for example, tetrabromo-*o*-xylene, $C_6H_4(CHBr_2)_2$, yields the compound $C_6H_4<\begin{matrix}CHBr\\CHBr\end{matrix}$; (3) union of two molecules, for example, ethyl bromomalonate yields ethyl ethanetetracarboxylate. Ethyl dibromomalonate yields ethyl ethylenetetracarboxylate. Benzophenone chloride yields dichlorotetraphenylethane, and benzophenone bromide yields tetraphenylethylene.

The following iodo-compounds have been prepared:

Amyl iodide, *iso*propyl iodide, trimethylene iodide, ethyl iodoacetate, *p*-nitrobenzyl iodide, *o*-, *m*-, and *p*-xylylene iodides. J. J. S.

Constitution of the Alcohols arising from the Condensation of Secondary Alcohols with their Sodium Derivatives. Marcel Guerbet (*Compt. rend.*, 1910, 150, 979—981. Compare Abstr., 1901, i, 307; this vol., i, 149).—The constitution of certain alcohols described in previous communications has been established by a study of their oxidation products. Dioctyl alcohol is shown to be η-methylpentadecan-ι-ol. *η-Methylpentadecan-ι-one* has b. p. 172—174°/21 mm., D 0·846, and forms a *semicarbazone*, m. p. 195—197° (corr.). Tri*sec.*-butyl alcohol is γ-methyl-ϵ-ethylnonan-η-ol. W. O. W.

Action of Organo-magnesium Compounds on Tiglic Aldehyde and the Optical Behaviour of the Products. Paul Abelmann (*Ber.*, 1910, 43, 1574—1588).—A number of unsaturated alcohols have been prepared by dropping tiglic aldehyde into an ethereal solution of magnesium ethyl bromide or the corresponding ethyl, propyl, *iso*propyl, *iso*butyl, or *iso*amyl bromides, and hydrolysing the resulting products. The yields vary from 40 to 70%. These alcohols can be transformed into the corresponding chlorides by boiling with concentrated hydrochloric acid according to Norris's method (Abstr., 1907, i, 1034), and into diolefine hydrocarbons,

$$CHMe:CMe\cdot CH:CHR,$$

by heating with potassium hydrogen sulphate or acetic anhydride and sodium acetate. The same hydrocarbons are formed by the action of quinoline on the chlorides, or by boiling the alcohols with hydrobromic acid. All the hydrocarbons are characterised by a high exaltation in their molecular refractions.

γ-Methyl-Δ^{β}-pentene-δ-ol, $CHMe:CMe\cdot CHMe\cdot OH$, has b. p. 55—56°/20 mm. or 84—86°/88 mm., or at 139—141°/760 mm. (slight decomp.). It has D^0 0·8793 and $n_D^{17\cdot5}$ 1·4428. The *acetate* has b. p. 153—155°, and the *chloride*, $C_6H_{11}Cl$, b. p. 41—43°/31 mm. *γ-Methylpentane-$\beta\gamma\delta$-triol*, $OH\cdot CHMe\cdot CMe(OH)\cdot CHMe\cdot OH$, obtained

by oxidising the alcohol with dilute permanganate, has b. p. 133—135°/13 mm. or 159—160°/41 mm., and solidifies when kept. The *triacetyl* derivative, $C_{12}H_{20}O_6$, has m. p. 123° and b. p. 143—146°/16 mm.

γ-Methyl-Δ$^{\beta}$-hexene-δ-ol, CHMe:CMe·CHEt·OH, has b. p. 71—73°/28 mm., 94—95°/80 mm., or 154—155°/760 mm., D^0 0·8857 and n_D^{10} 1·44914. The *acetate* has b. p. 167—170°, and the *chloride*, $C_7H_{13}Cl$, b. p. 51°/11·5 mm.

γ-Methylhexane-βγδ-triol, OH·CHMe·CMe(OH)·CHEt·OH, has b. p. 163°/36 mm., and yields a *triacetate*, $C_{13}H_{22}O_6$, b. p. 146—147°/12 mm.

γ-Methyl-Δ$^{\beta}$-heptene-δ-ol, CHMe:CMe·CPr·OH, has b. p. 74—77°/17 mm., D^0 0·8814, and n_D^{10} 1·45614. The *acetyl* derivative, $C_{10}H_{18}O_2$, has b. p. 79—83°/16 mm., and the *chloride*, $C_8H_{15}Cl$, b. p. 53—54°/11 mm.

γε-Dimethyl-Δ^{3}-hexene-δ-ol, CHMe:CMe·CH(OH)·CHMe$_2$, has b. p. 66—71°/19 mm. or 86—88°/42 mm., D^0 0·8727, and n_D^{10} 1·45214. The *acetate*, $C_{10}H_{18}O_2$, has b. p. 103—106°/57 mm., and the *chloride*, $C_8H_{15}Cl$, b. p. 58—60°/21 mm.

γζ-Dimethyl-Δ^{3}-heptene-δ-ol, CHMe:CMe·CH(OH)·CH$_2$·CHMe$_2$, has b. p. 113—114°/70 mm., D^0 0·8753, and $n_D^{9.6}$ 1·45337. The *acetate*, $C_{11}H_{20}O_2$, has b. p. 92—95°/18 mm., and the *chloride*, $C_9H_{17}Cl$, b. p. 59—63°/9 mm.

γη-Dimethyl-Δ$^{\beta}$-octene-δ-ol, CHMe:CMe·CH(OH)·CH$_2$·CH$_2$·CHMe$_2$, has b. p. 113—114°/30 mm., D^0 0·8762, and n_D^{10} 1·45460. The *acetate*, $C_{12}H_{22}O_2$, has b. p. 159—163°/80 mm., and the *chloride*, $C_{10}H_{19}Cl$, b. p. 83—84°/12 mm.

γ-Methyl-Δ$^{\beta\delta}$-pentadiene, CHMe:CMe·CH:CH$_2$, has b. p. 76—79°, D^0 0·7576, and $n_D^{16.5}$ 1·45427

αβγδ-Tetrabromo-γ-methylpentane, CHBrMe·CBrMe·CHBr·CH$_2$Br, is an unstable liquid, as is also the *dihydrobromide*, $C_6H_{12}Br_2$.

γ-Methyl-Δ$^{\beta\delta}$-hexadiene, CHMe:CMe·CH:CHMe, has b. p. 107—108°, D^0 0·7753, n_D^{15} 1·46146; *γ-methyl-Δ$^{\beta\delta}$-heptadiene*, CHMe:CMe·CH:CHEt, has b. p. 132—135°, D^0 0·7783, and $n_D^{14.7}$ 1·46493. The *dihydrobromide*, $C_8H_{16}Br_2$, has b. p. 109—110°/16 mm. *γε-Dimethyl-Δ$^{\beta\delta}$-hexadiene*, CHMe:CMe·CH:CMe$_2$, has b. p. 114—115°, D^0 0·7714, and $n_D^{16.5}$ 1·45457; the *dihydrobromide*, $C_8H_{16}Br_2$, has b. p. 99—103°/16 mm.

γζ-Dimethyl-Δ$^{\beta\delta}$-heptadiene, CHMe:CMe·CH:CH·CHMe$_2$, has b. p. 144—146°, D^0 0·7853, and n_D^{14} 1·46335. The *dihydrobromide*, $C_9H_{18}Br_2$, has b. p. 129—130°/20 mm.

γη-Dimethyl-Δ$^{\beta\delta}$-octadiene, CHMe:CMe·CH:CH·CH$_2$·CHMe$_2$, has b. p. 164—167°, D^0 0·7939, and $n_D^{14.5}$ 1·46650. The *dihydrobromide*, $C_{10}H_{20}Br_2$, has b. p. 136—139°/18 mm. J. J. S.

Modification of Couturier and Meunier's Process for the Preparation of Pinacone. A. H. Richard and Paul Langlais (*Bull. Soc. chim.*, 1910, [iv], 7, 454—458).—The process depends on the action of acetone on magnesium amalgam, the compound $Mg<^{O\cdot CMe_2}_{O\cdot CMe_2}$ being first formed, and yielding pinacone hydrate on addition of water (Abstr., 1902, i, 335; 1905, i, 326).

The modification consists in using commercial acetone instead of the pure ketone, and in employing acetone to wash out the pinacone in place of boiling water. It is unnecessary to maintain an atmosphere of dry carbon dioxide in the flask if the process is carried out rapidly. The yield of pinacone varies from 60 to 70% of the theoretical. The other products formed are *iso*propyl alcohol, mesityl oxide, *iso*phorone, a viscous *dihydric alcohol*, $C_6H_{14}O_2$, b. p. 100—108°/17 mm. or 196°/760 mm., and a *trihydric alcohol* (*βγε-trimethylhexan-βγε-triol*), $OH\cdot CMe_2\cdot CMe(OH)\cdot CH_2\cdot CMe_2\cdot OH$, b. p. 150—155°/20 mm., which has been synthesised by Bouveault and Levallois by the action of magnesium methyl iodide on methyl citramalate.

The exact working conditions and particulars of the isolation of these products are given in the original. T A. H.

Oxidation of Δγ-Acetylenic Glycols. Synthesis of α-Hydroxy-acids. Georges Dupont (*Compt. rend.*, 1910, **150**, 1523—1525. Compare this vol., i, 85).—Oxidation of Δγ-acetylenic glycols of the type $HO\cdot CRR'\cdot C{:}C\cdot CRR'\cdot OH$ by means of potassium permanganate results in the formation of α-hydroxy-acids; the yields, however, are not good, since further oxidation takes place, resulting, with tertiary glycols, in the production of oxalic acid and a ketone.

βε-Dimethyl-Δγ-hexinen-βε-diol yields α-hydroxy*iso*butyric acid, whilst *ββεε-tetraphenyl-Δγ-butinen-βε-diol*, $OH\cdot CPh_2\cdot C{:}C\cdot CPh_2\cdot OH$, m. p. 149—150°, obtained by the action of benzophenone on magnesium acetylene dibromide, gives diphenylglycollic acid with oxalic acid and benzophenone.

The yields are improved by employing the diacetates of the glycols. W. O. W.

Alkaline Hydrolysis of Glyceryl Trinitrate. Ernst Berl and Max Delpy (*Ber.*, 1910, **43**, 1421—1429).—The authors have hydrolysed an alcoholic solution of glyceryl trinitrate at 4° with alcoholic potassium hydroxide, and from the products have obtained ammonia, potassium nitrite and nitrate, carbon dioxide, hydrogen cyanide, oxalic acid, mesoxalic acid, αα-glyceryl dinitrate, and unchanged glyceryl trinitrate. C. S.

General Method for the Direct Preparation of Thiols from Alcohols by Catalysis. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1910, **150**, 1217—1221. Compare this vol., i, 294).—When the vapour of an alcohol mixed with hydrogen sulphide is passed over heated thorium oxide, a thiol is produced; the reaction is represented as: (1) $ThO_2 + 2C_nH_{2n+1}\cdot OH = ThO(OC_nH_{2n+1})_2 + H_2O$; (2) $ThO(OC_nH_{2n+1})_2 + 2H_2S = ThO_2 + 2C_nH_{2n+1}\cdot HS + H_2O$. A sulphide is formed in small quantity and with greater difficulty: $ThO(OC_nH_{2n+1})_2 + 2C_nH_{2n+1}\cdot HS = ThO_2 + 2(C_nH_{2n+1})_2S + H_2O$. The thorium oxide acts as a catalyst, and the action is continuous. The hydrogen sulphide employed need not be free from hydrogen.

An excellent yield of the corresponding thiols has been obtained from methyl, ethyl, propyl, *iso*butyl, *iso*amyl, and allyl alcohols, keeping the catalyst at 300—360°. Benzyl alcohol gave a good yield of

thiol, accompanied by the normal sulphide and some stilbene. In the case of secondary alcohols, the yields are less satisfactory; the following compounds have been prepared: propan-β-thiol; *cyclo*hexanethiol, b. p. 155° (compare Mailhe and Murat, this vol., i, 374); *2-methylcyclohexanethiol*, b. p. 161°; 3-methyl*cyclo*hexanethiol, b. p. 168°; *4-methylcyclohexanethiol*, b. p. 169°.

Thiophenols may be prepared by this method at 430—480°, but in no case does the yield exceed 17%. At 450°, phenol gives a small amount of diphenyl ether. W. O. W.

Formation of Acetic and Formic Acids by the Hydrolysis of Substances Containing Lignin. William E. Cross (*Ber.*, 1910, **43**, 1526—1528).—Acetic and formic acids are produced when substances rich in lignin are hydrolysed with 1% sulphuric acid at 130°, or even 110°.

The substances used were straw, jute, and various woods. Cellulose does not yield volatile acids, and pentosans but very little, so that the acids come from the lignin. It would thus appear that lignin contains acetyl and formyl groups, in addition to methoxy-groups.

With pine wood, the ratio acetic : formic acid is 4 : 1. J. J. S.

Simple Preparation of a Crystalline Ferric Acetate. Rudolf F. Weinland and Ernst Gussmann (*Zeitsch. anorg. Chem.*, 1910, **67**, 250—252).—When concentrated solutions of ferric chloride (1 mol.) and sodium acetate (3 mols.) are mixed and allowed to evaporate slowly, large, dark red prisms of ferric acetate are obtained. The addition of sodium platinichloride produces a characteristic precipitate of hexa-acetotriferric platinichloride (this vol., i, 296). The red salt is a compound of the mono- and di-acetate of this base:

$$\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]OAc,\left[Fe_3\begin{matrix}(OAc)_3\\OH_2\\OH\end{matrix}\right](OAc)_2,2H_2O.$$

Lithium chloride forms with this solution a *salt*:

$$2\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]Cl,\left[Fe_2\begin{matrix}(OAc)_6\\OH_2\\OH\end{matrix}\right](OAc)_2,14H_2O.$$

C. H. D.

Mixed Compounds of Salts and Anhydrides of Fatty Acids. Demetrius E. Tsakalotos (*Bull. Soc. chim.*, 1910, [iv], **7**, 461—464).—Franzen has shown (Abstr., 1908, i, 937) that compounds, analogous to Gerhardt's compound of potassium acetate and acetic anhydride, may be obtained with other acetates, and that for sodium and potassium two series of such products exist, represented by the formulæ: $Ac_2O,2CH_3\cdot CO_2M'$ and $Ac_2O,CH_3\cdot CO_2M'$. It is now shown that compounds analogous with those represented by the second formula may be obtained with acetic anhydride and the salts of the homologues of acetic acid, but that compounds represented by the first formula are not obtainable in these cases. The substances obtained crystallise

well, possess rhombic symmetry, and show marked double refraction. On exposure to the air, the crystals are transformed in a few minutes into microscopic cubes, and, when warmed at 80°, become isotropic without losing their form. The isotropic crystals melt at 150°; on further heating, the liquor effervesces and then passes into anisotropic crystals, which finally change at a higher temperature into amorphous solids. The original compounds probably have the general formula $Ac_2O{\cdot}O(CO{\cdot}R)M'$, and the first change from anisotropic to isotropic crystals probably accompanies a change represented by the equation: $R{\cdot}CO_2M'(CH_3CO)_2O \longrightarrow (R{\cdot}CO_2M')_2(CH_3CO)_2O$. The substances are obtained by boiling the appropriate salt with acetic anhydride during twenty minutes, filtering, and cooling, when colourless needles of the desired products are deposited. *Compounds* with the following salts are described.

Sodium formate.—This softens and becomes opaque at 82°, begins to clear at 114°, melts at 154°, effervesces at 174°, and re-solidifies at 185°. *Sodium propionate.*—This softens at 80°, melts at 154°, effervesces at 174°, and re-solidifies at 185°. *Sodium butyrate.*—This melts at 155°, effervesces at 180°, and re-solidifies at 188—190°.

Sodium valerate.—This, on heating, undergoes the series of changes mentioned under sodium formate at the following corresponding temperatures 82°, 154°, 175°, 180°. Exposed to the air this compound forms a mixture of isotropic cubes, crystalline substances, and isotropic droplets; the last of these eventually form monoclinic crystals showing extinction at about 45°, and analogous to sodium acetate crystals.

T. A. H.

Preparation of Pivalic Acid. A. H. Richard and P. Langlais (*Bull. Soc. chim.*, 1910, [iv], 7, 464—468).—Tiemann and Semmler have shown (Abstr., 1898, i, 629) that methyl ketones on oxidation by sodium hypobromite furnish bromoform and acids containing one carbon atom less than the parent ketones, and Denigès has confirmed this behaviour for pinacolin (Abstr., 1903, i, 606). This process has now been applied to pinacolin for the preparation of pivalic acid, of which a yield equal to 70% of the theoretical was obtained. Full details of the method of preparation are given in the original. The by-products are unchanged pinacolin, bromoform, carbon tetrabromide, tribromopinacolin, and trimethyl-lactic acid. The last-mentioned substance probably originates through the formation of some dibromopinacolin, which by the action of alkali would pass into trimethylpyruvic acid, and this, by the further action of alkali, would furnish trimethyl-lactic acid (compare Wittorff, Abstr., 1900, i, 422), and a trial with dibromopinacolin under the conditions prescribed confirmed this view. Boesekon has described already this method of preparing pivalic acid, but his observation that *iso*butyric acid is a by-product could not be confirmed.

T. A. H.

Some Salts of Gallipharic Acid, a Fatty Acid obtained by the Oxidation of *cyclo*Gallipharic Acid. Hermann Kunz-Krause and Paul Manicke (*Arch. Pharm.*, 1910, 248, 294—302).—An examination of the following salts of gallipharic acid confirms the

supposition previously advanced (Abstr., 1904, i, 587), that this acid is a pentadecanecarboxylic acid, $C_{15}H_{31}\cdot CO_2H$. *Sodium* salt, $C_{16}H_{31}O_2Na$; *potassium* salt; *potassium hydrogen* salt, $C_{16}H_{31}O_2K,C_{16}H_{32}O_2$, m. p. 103°; *calcium* and *barium* salts; *calcium hydrogen* salt, $(C_{16}H_{31}O_2)_2Ca,2C_{16}H_{32}O_2$, m. p. 87°; *barium hydrogen* salt, $(C_{16}H_{31}O_2)_2Ba,2C_{16}H_{32}O_2$, m. p. 98°; *cadmium* salt, m. p. 125—140°; *cadmium hydrogen* salt, $(C_{16}H_{31}O_2)_2Cd,2C_{16}H_{32}O_2$, m. p. 98·5°; *silver* salt; *silver hydrogen* salt, $2C_{16}H_{31}O_2Ag,C_{16}H_{32}O_2$; *copper* salt; *copper hydrogen* salt, $(C_{16}H_{31}O_2)_2Cu,C_{16}H_{32}O_2$, m. p. 98°; *ferric* salt, m. p. 78°; basic *lead* salt, $10(C_{16}H_{31}O_2)_2Pb,Pb(OH)_2$.

C. S.

Isomerisation of Oleic Acid by Displacement of the Double Linking. Albert Arnaud and Swigel Posternak (*Compt. rend.*, 1910, **150**, 1525—1528).—The reaction of Saytzeff (Abstr., 1887, 386), in which oleic acid is treated with hydrogen iodide and the product boiled with alcoholic potassium hydroxide, gives rise to a mixture containing at least four acids. In addition to regenerated oleic acid there is formed hydroxystearic acid, m. p. 83—84°, *Δ^{η}-elaidic acid*, and Δ^{θ}-elaidic acid. The separation of these acids is described, and Saytzeff's *iso*oleic acid shown to be a mixture.

Δ^{η}-Elaidic acid has also been obtained by partial hydrogenation of the corresponding stearolic acid by the method described previously (this vol., i, 356). The compound occurs in tablets, m. p. 53°, and yields a *dihydroxystearic acid*, crystallising in elongated laminæ, m. p. 98·5°.

W. O. W.

Two New Isomerides of Stearolic Acid. Albert Arnaud and Swigel Posternak (*Compt. rend.*, 1910, **150**, 1245—1247. Compare Abstr., 1909, i, 630; this vol., i, 356).—When fused stearolic acid is saturated with hydrogen iodide an oily mixture containing two isomeric di-iodostearic acids is produced. On hydrolysis this yields the original stearolic acid, together with two new isomerides crystallising in pearly lamellæ, and a monoiodo-acid, which resists further hydrolysis. *Δ^{η}-Stearolic acid*, m. p. 47·5°, yields suberic acid on oxidation, and unites with iodine, forming *$\theta\iota$-di-iodoelaidic acid*, needles, m. p. 67°. *Δ^{ι}-Stearolic acid*, m. p. 47°, yields sebacic acid on oxidation, and furnishes *$\iota\kappa$-di-iodoelaidic acid*, lamellæ, m. p. 45°; *κ-ketostearic acid* crystallises in rhombic lamellæ, m. p. 73·5°.

The iodoelaidic acids, m. p. 23—24° and 39°, described in a previous paper are now shown to be *θ*-iodo-Δ^{θ}-elaidic acid and *ι*-iodo-Δ^{θ}-elaidic acid respectively.

W. O. W.

Preparation of Aqueous Soluble Compounds from the Anhydrides of Hydroxymercurycarboxylic Acids. Walter Schoeller and Walther Schrauth (D.R.-P. 221483).—When the hydroxymercurycarboxylic anhydrides of the general formula

$$\underset{|\_\_\_\_|}{Hg\cdot A\cdot CO\cdot O},$$

where A is an aliphatic or aromatic residue, are slowly added to an aqueous solution containing molecular equivalents of alkali sulphite,

thiosulphate, or hyposulphite, and the mixture evaporated under reduced pressure, soluble products which are suitable for therapeutic employment are obtained.

The *product*, $ONa{\cdot}SO_2{\cdot}S{\cdot}Hg{\cdot}CH_2{\cdot}CO_2Na$, from hydroxymercuryacetic anhydride and sodium thiosulphate contains 48·07% Hg, whilst hydroxymercurybenzoic anhydride and sodium sulphite yield the *compound*, $NaO{\cdot}SO_2{\cdot}Hg{\cdot}C_6H_4{\cdot}CO_2Na$, containing 44·84% Hg.

F. M. G. M.

Action of Halogen Acids on Glycidic Esters. Georges Darzens (*Compt. rend.*, 1910, **150**, 1243—1245. Compare Abstr., 1905, i, 116).—Hydrogen chloride combines with ethyl $\beta\beta$-dimethylglycidate in cold ethereal solution, forming *ethyl β-chloro-α-hydroxyisovalerate*, $C_7H_{13}O_3Cl$, a substance with an unpleasant odour, m. p. 31—32°, b. p. 96—98°/20 mm. Ethyl $\alpha\beta\beta$-trimethylglycidate and hydrogen chloride form *ethyl β-chloro-α-hydroxy-α-methylisovalerate*, $C_8H_{15}O_3Cl$, b. p. 104—106°/21 mm. Hydrogen bromide yields the corresponding *bromo*-derivative, m. p. 21—22°, b. p. 100—105°/18 mm.

Hydrogen iodide converts glycidic esters into esters of the corresponding unsaturated acids; thus, ethyl $\beta\beta$-dimethylglycidate undergoes reduction to dimethylacrylic acid. It is essential for the success of the foregoing reactions that the materials should be perfectly dry. W. O. W.

Action of Ethyl Sodiomalonate on ακ-Dibromodecane. Adolf Franke and Oswald Hankam (*Monatsh.*, 1910, **31**, 177—189).—ακ-Dibromodecane reacts with ethyl sodiomalonate, yielding a product which appears to be ethyl *cyclo*undecane-1 : 1-dicarboxylate, $\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\end{matrix}\!>\!C(CO_2Et)_2$. A by-product, formed at the same time, appears to be ethyl dodecanetetracarboxylate,

$$CH(CO_2Et)_2{\cdot}[CH_2]_{10}{\cdot}CH(CO_2Et)_2.$$

Decane-ακ-diol, prepared by Bouveault and Blanc's method (Abstr., 1903, i, 731), reacts with fuming hydrobromic acid at 60° in sealed tubes, yielding *ακ-dibromodecane*, $C_{10}H_{20}Br_2$, which crystallises in colourless plates, m. p. 27°.

Ethyl cyclo*undecanedicarboxylate*, $C_{17}H_{30}O_4$, is a colourless, viscid liquid, b. p. 200—220° under reduced pressure. The corresponding *acid*, $C_{13}H_{22}O_4$, forms a fatty solid, m. p. 75°, and does not combine with bromine; the *potassium* salt is gelatinous, and the *silver* and *calcium* salts form colourless precipitates.

When heated at 130—150° the dibasic acid loses carbon dioxide and yields cyclo*undecanecarboxylic acid*, $C_{11}H_{21}{\cdot}CO_2H$, which is also a fatty solid, m. p. 94—96°.

Ethyl dodecanetetracarboxylate, $C_{24}H_{42}O_8$, has b. p. 250—265° under reduced pressure; the corresponding *acid*, $C_{16}H_{26}O_8$, crystallises from water, and has m. p. 128°, but when heated at 160—170° loses carbon dioxide and yields *dodecanedicarboxylic acid*, $CO_2H{\cdot}C_{12}H_{24}{\cdot}CO_2H$, which also crystallises from water, and has m. p. 123°. J. J. S.

Arabonic Acid. K. H. Böddener and Bernhard Tollens (*Ber.*, 1910, **43**, 1645—1650 *).—Guerbet's method of obtaining *d*-arabinose

* and *Zeitsch. Ver. deut. Zuckerind*, 1910, 727—738.

by heating a solution of mercuric gluconate (Abstr., 1908, i, 123) has been applied to mercuric *l*-arabonate, whereby a poor yield of *l*-erythrose has been obtained.

A freshly prepared solution of arabonolactone has $[\alpha]_D$ about 70°, and one of arabonic acid has $[\alpha]_D$ −10°; both solutions in course of time attain to the same value, $[\alpha]_D$ −51·5°. This behaviour, which is also exhibited by gluconic acid, galactonic acid, rhamnonic acid, and their lactones, appears to be a characteristic property of acids of the sugar group, and can be utilised for their identification.

Methyl arabonate, obtained by keeping a solution of arabonolactone in somewhat diluted methyl alcohol over lime or by heating calcium arabonate, methyl alcohol, and sulphuric acid on the water-bath, exhibits an initial rotation, $[\alpha]_D$ −6·7°, which changes to −42·7° by keeping, the change being due to the gradual decomposition of the ester into the acid and methyl alcohol. C. S.

Formation of Lævulic Acid from Hexoses. William Alberda van Ekenstein and Jan J. Blanksma (*Chem. Weekblad*, 1910, **7**, 387—390).—There are two stages in the formation of lævulic acid from hexoses: hydroxymethylfurfuraldehyde is first formed by elimination of water, and is subsequently transformed into lævulic acid and formic acid. Ihl and Pechmann's test for hexoses is explained by the fact that warming hydroxymethylfurfuraldehyde with diphenylamine yields a substance of dark blue colour. A. J. W.

Action of the Electric Discharge on Acetaldehyde in Presence of Hydrogen. Adolphe Besson and A. Fournier (*Compt. rend.*, 1910, **150**, 1238—1241. Compare Losanitsch, this vol., i, 1).—When the vapour of acetaldehyde mixed with a small amount of hydrogen is submitted to the action of the silent electric discharge, a brilliant phosphorescence is produced, and a liquid formed having an odour of pickled herrings. This has been found to contain acetic acid and homologous acids, acetone, diethyl ketone, diacetyl, unidentified viscous substances, and an acid, $C_4H_8O_3$, having the properties of *β*-hydroxybutyric acid. W. O. W.

α-Bromocrotonaldehyde. P. L. Viguier (*Compt. rend.*, 1910, **150**, 1431—1433. Compare Abstr., 1909, i, 691).—The constitution of α-bromocrotonaldehyde has been proved by its oxidation to α-bromocrotonic acid. A more rapid method for preparing the substance than that previously described consists in brominating crotonaldehyde and adding the product to a 50% solution of sodium acetate at 150—170°. The aldehyde is separated by distillation in steam. When heated with pyridine and malonic acid, it yields *γ-bromosorbic acid*,

$$CHMe{:}CBr{\cdot}CH{:}CH{\cdot}CO_2H,$$

m. p. 133°; the *potassium* salt forms pearly lamellæ (compare Riedel and Straube, Abstr., 1909, i, 550). The cyanohydrin decomposes when distilled in a vacuum; on hydrolysis, it yields *β-bromo-α-hydroxy-Δ^{β}-pentenoic acid*, $CHMe{:}CBr{\cdot}CH(OH){\cdot}CO_2H$, m. p. 123—124°; the *potassium* salt crystallises in prisms, the *silver* salt in long, brilliant needles. W. O. W.

Production of Aldehyde Resins by the Carbonisation of Wood in Closed Vessels. René P. Duchemin (*Bull. Soc. chim.*, 1910, [iv], 7, 473—479).—A résumé is first given of the work of Kleeberg (Abstr., 1891, 1199), Trillat (*Annalen*, 1891, 263, 312), Blumer (Fr. Pat. 329982 of 1903), Delaire (Fr. Pat. 361509 of 1905), Baekeland (*Mon. Sci.*, 1909, 421) and others on the condensation of formaldehyde with phenols in the presence of alkalis or acids to form resinous products, which in some cases resemble copal or lac.

In connexion with the investigation of a new process of manufacturing crude acetates (Fr. Pat. 375314 and 402907 of 1908), the author has observed the formation of similar resins in passing the acid vapours from the distillation of wood, first through an apparatus for the removal of tar, and then into scrubbers containing alkaline liquids. The latter are at first brown or black, but become golden-yellow as the passage of the vapours continues, and finally deposit black, plastic masses, which after heating at 200° become hard and possess a conchoidal fracture. Similar products are obtained by (1) heating crude pyroligneous acid under a reflux condenser, (2) condensing "heavy oils" recovered from crude pyroligneous acid with formaldehyde in presence of hydrochloric acid, (3) heating the mother liquors recovered from the manufacture of crude acetates, and then adding water. These products have m. p. 60—70°, dissolve in alkaline solutions, and are re-precipitated by acids. They are soluble in acetone, wood-spirit, or methyl acetate, but the extent of their solubility depends on the temperature to which they have been heated. These resins probably result from the interaction of aldehydic with phenolic substances, both these groups of products occurring in the vapours from the distillation of wood. It is suggested that wood tar may consist of a solution of these resins in phenols (compare Lingner, Fr. Pat. 328971 of 1903).

The resins obtained in distilling wood-spirit over alkalis differ from the foregoing in their lighter colour and in being insoluble in alkalis.

T. A. H.

Preparation of Pinacolin. A. H. Richard and P. Langlais (*Bull. Soc. chim.*, 1910, [iv], 7, 459—461).—The preparation was effected (1) by heating pinacone hydrate with a 30% solution of sulphuric acid during three hours at 150° and steam-distilling the mixture, or (2) by heating pinacone hydrate with dry oxalic acid in a calcium chloride bath. The first process gave a 90%, and the second a 75% yield of crude pinacolin. The oxalic acid was used several times, but eventually became coated with tarry matters and had to be replaced by fresh material.

On fractionation, the crude pinacolin yielded, as more volatile by-products, acetone and di*iso*propenyl (Couturier, Abstr., 1893, i, 244; Kondakoff, Abstr., 1901, i, 62), and, as less volatile by-products, unaltered pinacone, mesityl oxide, and *iso*phorone. The di*iso*propenyl probably resulted from complete dehydration of pinacone, but the mesityl oxide and *iso*phorone were probably present as impurities in the pinacone hydrate used (see this vol., i, 455), and the acetone and a

small quantity of mesitylene found probably resulted from the action of acids on these impurities. T. A. H.

Reduction of Aliphatic Diketones. Edmond E. Blaise and A. Kœhler (*Bull. Soc. chim.*, 1910, [iv], 7, 416—420).—In a previous paper (Abstr., 1909, i, 204) it has been shown that aliphatic diketones can be synthesised by the action of the chlorides of dibasic acids on mixed organic compounds of zinc. Perkin has observed (Trans., 1891, 59, 214) that nonane-$\beta\theta$-dione on reduction with sodium yielded a cyclic pinacone, and it was therefore of interest to ascertain within what limits the formation of a ring depends on the relative positions of the two carbonyl groups. Reduction of octane-$\beta\eta$-dione, decane-$\gamma\theta$-dione, and undecane-$\gamma\iota$-dione furnished no cyclic pinacones, but only the corresponding glycols, and, similarly, attempts to dehydrate undecane-$\gamma\iota$-diol were unsuccessful.

Octane-$\beta\eta$-dione, on reduction by Perkin's method (*loc. cit.*), yielded the secondary cyclic alcohol already described by Perkin (Trans., 1890, 57, 245), and *octane-$\beta\eta$-diol*, b. p. 138—139°/15 mm., a viscous liquid with a sweetish acrid taste, and readily soluble in organic solvents; its *diphenylurethane*, m. p. 126°, crystallises in long needles from a mixture of light petroleum and ether.

Decane-$\gamma\theta$-dione under similar conditions yielded a *hydrocarbon*, b. p. 70—72°/11 mm., and the corresponding *glycol*, m. p. 72°, which crystallises in silky needles from a mixture of ether and light petroleum. The *diphenylurethane*, m. p. 137°, crystallises from ether in needles, and is greasy to the touch. Undecane-$\gamma\iota$-dione furnished a trace of pinacone (?), b. p. 156°/18 mm., and the corresponding *glycol*, m. p. 80·5°, crystallising from warm ether in long, silky needles. The *diphenylurethane*, m. p. 84—85° (approx.), crystallises from a mixture of benzene and light petroleum in splendid needles. T. A. H.

New Synthesis of Natural and Racemic Erythritol. H. Pariselle (*Compt. rend.*, 1910, 150, 1343—1346. Compare Abstr., 1909, i, 691; Lespieau, Abstr., 1907, i, 173).—Δ^{α}-Butylene-$\gamma\delta$-oxide, $\begin{matrix}CH_2\\ |\\ O\end{matrix}\!\!>\!CH\cdot CH{:}CH_2$, prepared by heating δ-bromo-Δ^{α}-butylene oxide with potassium hydroxide, is a very mobile liquid, b. p. 70°/760 mm., D^0 0·9006, D^{20} 0·87, n_D^{20} 1·416. When shaken with water and a few drops of sulphuric acid, a solid polymeride is formed, and the solution, on distillation in a vacuum, yields erythrol (Δ^{α}-butylene-$\gamma\delta$-diol), $OH\cdot CH_2\cdot CH(OH)\cdot CH{:}CH_2$, as a syrupy liquid, b. p. 91—93°/12 mm., D^{14} 1·05, n_D^{14} 1·469; the *diphenylurethane* has m. p. 125—126°. When the diol is treated with barium permanganate, a syrup is obtained, which deposits natural erythritol when sown with a crystal of this substance. The residual liquid contains racemic erythritol, isolated and identified by conversion into the dibenzoylacetal. W. O. W.

Aloinose, the Sugar from Aloin. Eugène Leger (*Compt. rend.*, 1910, 150, 983—986; *Bull. Soc. chim.*, 1910, [iv], 7, 479—485. Compare Abstr., 1903, i, 356; 1904, i, 907).—Further experimental

details are given for the preparation of aloinose from barbaloin. The sugar has $[\alpha]_D$ 57·3° to 58·5°, and forms an *osazone*, crystallising in elongated, pointed lamellæ.

On hydrolysis with alcoholic sulphuric acid, nataloin yields small quantities of a non-crystalline, lævorotatory sugar closely resembling aloinose. W. O. W.

Nitration of Cotton Wool. Cellulose. Piest (*Zeitsch. angew. Chem.*, 1910, 23, 1009—1018).—A résumé of previous work on cellulose and its nitrates is given. The action of various alkalis on gun-cottons prepared in different ways has been investigated.

Gun-cotton prepared from cotton wool treated in the usual manner gave a residue of 8% when left in contact with 0·5*N*-sodium hydroxide solution during ten days, whereas a gun-cotton prepared from a strongly bleached cotton wool left a residue of only 1·7% insoluble matter, after similar treatment during four days. Gun-cotton prepared from mercerised cotton gave a residue of 13% after ten days. Similar experiments with a concentrated ammonium sulphide solution gave a residue of 49·5% after eight days using ordinary gun-cotton, a residue of 37·5% with gun-cotton from strongly bleached cotton, and 52% with a gun-cotton from mercerised cotton. Treatment of a gun-cotton with alkalis affords a method for determining the manner in which the cotton had been treated before nitration.

The resistance of various gun-cottons towards alkalis is in the order of the resistance of the materials from which they were obtained.

The action of alkalis on collodion wools prepared from samples of cotton wool which have been subjected to different treatment has also been examined, and the results obtained are similar to those with gun-cottons. When concentrated ammonium sulphide is used, complete hydrolysis is brought about in four days, since the residue left contains no nitrogen.

During nitration, especially when the amount of water present is large, hydroxycelluloses are formed, and the final products are mixtures of esters of cellulose and hydroxycelluloses.

Treatment of the esters with ammonium sulphide appears to bring about a partial conversion of cellulose into hydroxycelluloses.

J. J. S.

Mercury Fulminate. Andreas Solonina (*Zeitsch. Schiess Sprengstoffwesen*, 1910, 5, 41—46, 67—72).—A discussion of the various methods usually employed for the preparation of mercury fulminate, with particulars of numerous experiments by the author, and microphotographs showing the crystalline structure of the products.

The second paper contains details of experiments for the purification of mercury fulminate for analysis; the employment of ammonia is not considered satisfactory, but the preparation of the crystalline compound with pyridine, its subsequent decomposition with water, and the final estimation of mercury by electrolysis is recommended.

F. M. G. M.

Calcium Cyanamide and some Compounds Prepared from it. Fr. Reis (*Biochem. Zeitsch.*, 1910, 25, 460—476).—Cyanamide in a state of purity is best prepared from calcium cyanamide by precipitation with the theoretical quantity of oxalic acid calculated from the calcium content of the calcium cyanamide. An alkaline solution of calcium cyanamide rapidly decomposes at the ordinary temperature, and still more rapidly on heating, dicyanodiamide in varying amounts being formed; an acid solution is, at the ordinary temperature, stable. Warm permanganate solution has practically no action; Devarda's alloy reduces the cyanamide rapidly to ammonia, and gives a large increase in the quantity of dicyanodiamide formed. The optimum conditions for the conversion into dicyanodiamide are obtained by the use of carbonates of the alkalis and alkaline earths at 65°. The decomposition undergone in the presence of soil may be due to bacterial action, if the concentration be not so great as to inhibit the action of the organisms. The presence of ferric oxide has the catalytic effect of accelerating the decomposition of cyanamide into carbamide. No compound of cyanamide and iron could be formed. G. S. W.

Cryohydrates of Ammonium and Potassium Thiocyanates. Alexis M. Vasilieff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 423—427).—The author has investigated the cryohydrates of these salts by Flawitzky's method of cooling mixtures. Ammonium thiocyanate forms the cryohydrate, $NH_4{\cdot}CNS,5{\cdot}851H_2O$, at $-25{\cdot}2°$, and the potassium salt, $KCNS,5{\cdot}349H_2O$, at $-31{\cdot}2°$; these compositions are in accord with Guthrie's law (this Journ., 1875, 530), the smaller proportion of water present in the cryohydrate corresponding with the lower temperature. The lower water-content of the cryohydrate of the potassium salt is also in agreement with the greater solubility of this salt. In the formation of these cryohydrates, the mixtures of salt and snow do not solidify, and the residues left in the refrigerator always consist solely of the excess of salt which has not taken part in the reaction, so that it is highly probable that the action occurs between the snow and anhydrous salt without formation of hydrates.

The m. p.'s of these thiocyanates were given by Pohl (1851) as 161·2° for the potassium salt and 159° for the ammonium salt, the latter figure being confirmed by Reynolds (this Journ., 1869, 1). The author obtains the m. p. 174·2° for the potassium salt, and 149·5° for the ammonium salt, but in the latter case decomposition occurs to some extent. Using these numbers, Flawitzky's law (Abstr., 1906, ii, 152) gives (1) for the ammonium salt, the relation between the polymerisations of the salt and water represented by $(H_2O)_6 : (NH_4{\cdot}CNS)_5$, and the composition of the cryohydrate, $NH_4{\cdot}CNS,5{\cdot}931H_2O$; and (2) for the potassium salt, the ratio $(H_2O)_4 : (KCNS)_5$, and the composition $KCNS,5{\cdot}332H_2O$ for the cryohydrate. If potassium and ammonium thiocyanates form a eutectic mixture, the constituents should be present in the proportion of 3 mols. to 2 mols. T. H. P.

Diastatic Scission of Lactose Derivatives. H. Bierry and Albert Ranc (*Compt. rend.*, 1910, 150, 1366—1368. Compare Abstr., 1908, i, 1031).—Lactoseaminoguanidine nitrate (Wolff, Abstr.,

1896, i, 78) has $[\alpha]_D^{20}$ 8·4°, and m. p. 225—227° on the Maquenne block. The digestive juice of snails hydrolyses this substance with formation of galactose and dextroseaminoguanidine. The same ferment decomposes lactosesemicarbazone into galactose and dextrosesemicarbazone, a similar fission occurring in the case of Schoorl's lactosecarbamide (*Rec. trav. chim.*, 1903, 22, 31).

The experiments support Fischer's view that lactose is the galactoside of dextrose. W. O. W.

Instability of Alloxan. Alvin S. Wheeler (*J. Amer. Chem. Soc.*, 1910, 32, 809).—A sample of alloxan, which had been kept for several years in a bottle, suddenly underwent spontaneous decomposition and caused a violent explosion. This behaviour does not appear to have been noticed previously.

Marston T. Bogert (*ibid.*, 809—810) records a similar explosion in a case containing alloxan amongst other fine organic chemicals.

E. G.

Formation of Hydrogen Cyanide. Armand Jorissen (*Bull. Acad. roy. Belg.*, 1910, 224—233).—The first part of the paper deals with the conclusions arrived at by the author and others concerning the production of hydrogen cyanide in plants (compare Jorissen, Abstr., 1885, 181; Jorissen and Hairs, Abstr., 1892, 502; Hébert, Abstr., 1899, ii, 377; Greshoff, Abstr., 1907, ii, 121; and Treub, *Ann. Jar. bot. Buitenzorg*, 1905, [ii], 4, 86).

Although Seyewetz and Poizat have recently shown (Abstr., 1909, i, 146) that a large number of aromatic compounds give hydrogen cyanide when boiled with a mixture of nitric and nitrous acids, this observation cannot be used in support of the hypothesis that the naturally occurring hydrogen cyanide is formed by the action of nitrates on organic substances, since the conditions are entirely different. The author, however, finds that a number of substances when acted on with dilute nitric acid at the ordinary temperature in the light, form appreciable quantities of hydrogen cyanide; thus when 0·5 to 1·0 gram of morphine, brucine, vanillin, quinol, catechol, resorcinol, sucrose, lactose, or honey is kept in contact with 100 c.c. of a 3·4% aqueous solution of nitric acid at the ordinary temperature and exposed to light, a small amount of hydrogen cyanide is formed. The reaction, like that described by Seyewetz and Poizat, is inhibited by carbamide, but is unaffected by asparagine. Addition of potassium nitrite solution to the nitric acid immediately after the addition of vanillin does not cause the instantaneous formation of hydrogen cyanide. E. H.

Application of Magnesium in Organic Chemistry. Victor Grignard (*Chem. Zeit.*, 1910, 34, 529; *Bull. Soc. chim.*, 1910, [iv], 7, 453—454).—In reply to Barbier (this vol., i, 308), the author mentions that he has in common with others, who have written on the application of magnesium in organic chemistry, referred to the importance in this connexion of Barbier's synthesis of dimethylheptenol by the use of magnesium methyl iodide. He adds, however,

that Barbier's method is a modification of the Saytzeff reaction, in which two substances merely react in presence of magnesium, whilst his own method is derived from the work of Frankland, Wanklyn, and Wagner on mixed organo-magnesium compounds and their application.

T. A. H.

*cyclo*Hexylallylene [*cyclo*Hexylpropylene] and *cyclo*Hexylpropinene. B. DE RESSÈGUIER (*Bull. Soc. chim.*, 1910, [iv], 7, 431—434).—*cyclo*Hexylpropylene, $C_6H_{11}\cdot CH_2\cdot CH{:}CH_2$, D^0 0·8312, D^{13} 0·8196, n_D^{13} 1·45362, b. p. 148—149°, prepared by the action of allyl bromide on magnesium *cyclo*hexyl bromide (compare Tiffeneau, Abstr., 1904, i, 872), is a colourless liquid of pleasant odour (compare Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 630). The *dibromide* has D^0 1·537 and b. p. 143—144°/16 mm. On treatment with potassium hydroxide in alcohol, it yields cyclo*hexylbromopropylene*,

$$C_6H_{11}\cdot CH_2\cdot CH{:}CHBr,$$

D^0 1·2063, b. p. 122—124°/17 mm., a colourless liquid, and finally cyclo*hexylpropinene*, b. p. 165—170°. The latter was not purified, but was converted into the sodium derivative, and the latter by the action of carbon dioxide transformed into cyclo*hexyltetrolic acid*,

$$C_6H_{11}\cdot CH_2\cdot C{:}C\cdot CO_2H,$$

m. p. 74—75°, which crystallises from carbon tetrachloride. The *methyl* ester has b. p. 135°/15 mm., D^0 1·010, D^{16} 0·9978, n_D^{12} 1·48354, corresponding with mol. ref. 51·41 in place of the calculated value 50·43 (compare Moureu, Abstr., 1906, ii, 1). T. A. H.

Freezing of Mixtures of Isomeric Benzene Derivatives. GIUSEPPE BRUNI (*Zeitsch. Elektrochem.*, 1910, 16, 285).—The phenomena described by Fischer (this vol., i, 309) are quite in accordance with the regularities observed by the author. In general, position isomerides in the benzene series do not form solid solutions, but substances having analogous substituting groups in the same position do.

T. E.

Derivatives of Ethylbenzene and of *iso*Propylbenzene. ERLING SCHREINER (*J. pr. Chem.*, 1910, [ii], 81, 557—564).—*p*-Chloroethylbenzene is readily obtained by heating ethyl bromide and chlorobenzene with aluminium chloride on the water-bath. An individual product is not obtained when bromobenzene is used. *o*- and *p*-Nitroethylbenzene are easily obtained by dissolving ethylbenzene in fuming nitric acid and fractionating the product under diminished pressure. By reduction with tin and hydrochloric acid, each yields the corresponding amino-derivative, from which by diazotisation and treatment with potassium iodide, o-*iodoethylbenzene*, b. p. 226°, D_4^{16} 1·6189, n_D 1·59408, and p-*iodoethylbenzene*, m. p. −11°, b. p. 230°, D_4^{16} 1·6095, n_D^{22} 1·59094, are obtained. The *iododichloride*, $C_6H_4Et\cdot ICl_2$, of the former, obtained by the direct action of chlorine at 0°, is an unstable, yellow, crystalline substance decomposing at 63°; treatment with sodium hydroxide yields, not the iodoso-compound, but the *iodonium hydroxide*, $I(C_6H_4Et)_2\cdot OH$, since the addition of potassium iodide to the solution yields the *iodide*, $(C_6H_4Et)_2I_2$, which decomposes at 126°.

p-Iodo*iso*propylbenzene, which can be prepared by heating *iso*propylbenzene, iodine, and iodic acid in slightly diluted acetic acid for six hours, forms a *iododichloride*, $C_6H_4Pr^{\beta}\cdot ICl_2$, a citron-yellow powder decomposing at 110°, from which the *iodoso*-compound, $C_6H_4Pr^{\beta}\cdot IO$, decomposing at 165° (the *acetate*, $C_6H_4Pr^{\beta}\cdot I(OAc)_2$, has m. p. 89°), the *iodoxy*-compound, exploding at 191°, and the iodonium *iodide*, decomposing at 140°, are readily obtained. C. S.

Phenylsulphoxyacetic Acid. II. Rudolf Pummerer (*Ber.*, 1910, **43**, 1401—1412. Compare Abstr., 1909, i, 580).—Phenylsulphoxyacetic acid is obtained by passing dry nitrous fumes into dry ethereal phenylthiolacetic acid; by the addition of petroleum, a brown oil separates, which evolves nitric oxide (?), and yields phenylsulphoxyacetic acid. *Phenylbenzylsulphoxide*, $CH_2Ph\cdot SOPh$, m. p. 125·5°, obtained in a similar manner from phenyl benzyl sulphide, does not yield thiophenol by heating with 50% sulphuric acid, and forms benzyl chloride and a little benzaldehyde with alcoholic hydrogen chloride. The preceding sulphoxides are also very conveniently prepared by the oxidation of phenylthiolacetic acid and phenyl benzyl sulphide by 33% hydrogen peroxide in glacial acetic acid. Diethyl sulphide is converted by this oxidising agent, with careful cooling, into diethyl sulphoxide, which forms with a solution of hydroferrocyanic acid, a stable, crystalline *hydroferrocyanide*, $C_4H_{10}OS,H_4Fe(CN)_6,H_2O$, which turns blue at 140°.

Phenylthiolacetic acid is converted by alcoholic hydrogen chloride into the ethyl *ester*, b. p. 144—145°/14 mm., an ethereal solution of which yields with sodium a yellowish-white, powdery sodio-derivative, which reacts with ethereal methyl iodide to form *ethyl α-phenylthiolpropionate*, $SPh\cdot CHMe\cdot CO_2Et$, b. p. 139·5°/14·5—15 mm., an ethereal solution of which also reacts with sodium.

α-Phenylthiolpropionic acid, obtained from α-bromopropionic acid and thiophenol in alkaline solution, is converted by cold hydrogen peroxide in glacial acetic acid into *α-phenylsulphoxypropionic acid*, $Ph\cdot SO\cdot CHMe\cdot CO_2H$, m. p. 135°, which is converted into thiophenol and pyruvic acid by boiling 25% sulphuric acid. The oxidation of ethyl phenylthiolacetate by 33% hydrogen peroxide and glacial acetic acid at 40—50° leads to the formation of *ethyl phenylsulphoxyacetate*, b. p. 152—154°/3 mm., a colourless, almost odourless, mobile liquid, which decomposes at 220—230°, yielding thiophenol and ethyl phenylthiolacetate and other products, is decomposed by cold fuming hydrochloric acid with the formation of thiophenol, and is easily hydrolysed by alcoholic potassium hydroxide, which, even when boiling, does not cause the generation of thiophenol.

A migration of oxygen from sulphur to carbon occurs when ethyl phenylsulphoxyacetate is heated with acetic anhydride, whereby *ethyl α-acetoxyphenylthiolacetate*, $SPh\cdot CH(OAc)\cdot CO_2Et$, b. p. 172·5°/15 mm., is formed. *Phenylthiolmethyl acetate*, $SPh\cdot CH_2\cdot O\cdot COMe$, b. p. 249°/713 mm., is obtained by heating phenylsulphoxyacetic acid with acetic anhydride, or, better, by the action of lead peroxide on phenylthiolacetic acid in boiling glacial acetic acid; it yields thiophenol very readily by treatment with alcoholic potassium hydroxide. C. S.

Distyrene. Carl Liebermann (*Ber.*, 1900, 43, 1543—1544).—The author agrees with Erlenmeyer (this vol., i, 309) that the compound described previously (Abstr., 1889, 1196) as distyrene is stilbene. J. J. S.

Triarylmethyls. IV. Wilhelm Schlenk, Anna Herzenstein, and Tobias Weickel (*Ber.*, 1910, 43, 1753—1758. Compare Abstr., 1909, i, 791; this vol., i, 236, 237).—Gomberg and Cone (Abstr., 1906, i, 414, 821) by the action of silver on ω-chlorophenyldiphenylenemethane in presence of air obtained phenyldiphenylenemethyl peroxide; in the absence of air a hydrocarbon was formed, which they could not isolate. When ω-chlorophenyldiphenylenemethane is heated in benzene with copper bronze or copper powder in an atmosphere of carbon dioxide, *diphenylbisdiphenylene-ethane*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CPh\cdot CPh\!<\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, is formed. This crystallises in long, obliquely-cut plates, m. p. 205—230° (decomp.), or when heated in sealed tubes in an atmosphere of carbon dioxide, m. p. 254°.

Solutions in organic solvents become more or less brown in colour on heating, the colour vanishing again on cooling. This change is attributed to dissociation into the methyl compound, $\cdot CPh\!<\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$; it is specially marked in anisole. The colourless solutions do not decolorise iodine solutions; the hot brown solutions rapidly decompose iodine solutions. Bisdiphenylbisdiphenylene-ethane (*loc. cit.*, 238) hardly shows any tendency to dissociate.

Phenylbisdiphenylmethyl, $CPh(C_6H_4\cdot C_6H_5)_2$, is now obtained as a colourless powder. This is only slowly soluble in benzene; the solution is at first colourless and then red. Molecular-weight determinations indicate that 80% of the compound is present as methyl derivative. E. F. A.

***s*-Dichlorotetraphenylethane.** Hans Finkelstein (*Ber.*, 1910, 43, 1533—1535. Compare Schmidlin and von Escher, this vol., i, 369).—*s*-Dichlorotetraphenylethane can be prepared by the action of sodium iodide on an acetone solution of ω-dichlorodiphenylmethane. If a large excess of the iodide is used, tetraphenylethylene is formed, but with a mixture of two parts of the chloro-derivative, 1·4 of sodium iodide, and 10 of acetone, a 75% yield of the dichlorotetraphenylethane can be obtained by keeping at the ordinary temperature for two days. The same product is formed by the addition of chlorine to tetraphenylethylene, although the unsaturated hydrocarbon does not combine with bromine. When heated alone or with indifferent solvents of high boiling point, hydrogen chloride is formed, together with impure tetraphenylethylene. The unsaturated hydrocarbon contains chlorine attached to one of the benzene nuclei.

When the dichloro-derivative is boiled with methyl alcohol, the chief product is β-benzopinacoline. J. J. S.

Preparation of Acylaminophenylsulphonamic Acids. Hugo Weil and Karl Weisse (D.R.-P. 221301).—Acylaminophenyl

sulphonamic acids and their homologues are readily prepared by heating acylnitroanilines with an aqueous solution of sodium hydrogen sulphite. By the action of halogens in aqueous alkaline solution on these compounds, substituted halogen derivatives are formed; from these the acyl and sulpho-groups are removed by heating with mineral acid and subsequent boiling with alkali hydroxide, yielding halogenated diamines.

If boiled with alkali, the acyl gronp only is removed, and on acidification the crystalline *anilinesulphonamic acid* is precipitated; this is readily diazotised, yielding *diazobenzenesulphonamic acid*, which by contact with dilute mineral acid is converted into diazo-*p*-aminobenzene. F. M. G. M.

Trinitro-*p*-anisidine. Frédéric Reverdin [with A. de Luc] (*Arch. Sci. phys. nat.*, 1910, [iv], 29, 476—483; *Compt. rend.*, 1910, 150, 1433—1435*).—When benzoyl-2 : 3-dinitro-*p*-anisidine (Abstr., 1909, i, 377) is nitrated with nitric acid (D 1·52), first at 5—10°, and then at 60° for five minutes, *nitrobenzoyl*-2 : 3 : 6-*trinitro*-p-*anisidine* is obtained as a felted mass of colourless, slender needles, m. p. 247°. When treated with three times its weight of strong sulphuric acid on the water-bath, it gives on cooling a brilliant red precipitate of the corresponding 2 : 3 : 6-*trinitro*-p-*anisidine*, m. p. 127—128°. From aqueous solutions large, reddish, orthorhombic crystals are obtained [$a : b : c = 0{\cdot}738287 : 1 : 0{\cdot}812027$]. The action of acetic anhydride in the presence of a small quantity of concentrated sulphuric acid gives the *acetyl* derivative, $C_9H_8O_8N_4$; white needles, m. p. 242°.

One of the nitro-groups (it is not certain which) in trinitro-*p*-anisidine is very reactive. When heated with excess of various bases, compounds of the general formula $OMe{\cdot}C_6H(NO_2)_2R{\cdot}NH_2$ are produced, R representing the residue of the base employed. The *aniline* derivative, $C_{13}H_{12}O_5N_4$, has m. p. 148°, and forms brown spangles; the p-*toluidine* derivative, $C_{14}H_{14}O_5N_4$, forms brown, prismatic crystals, m. p. 139°; the *monomethylamine* derivative, $C_8H_{10}O_5N_4$, crystallises in reddish-violet needles, m. p. 199—200°.

When trinitro-*p*-anisidine is heated in alcoholic solution with sodium acetate, a reddish-brown precipitate of the sodium salt of a *dinitrohydroxy*-p-*anisidine*, $OMe{\cdot}C_6H(NO_2)_2(OH){\cdot}NH_2$, is obtained. On the addition of acid to the aqueous solution of this salt, brown needles of the dinitrohydroxy-*p*-anisidine are obtained, m. p. 161°. The *acetyl* derivative is obtained by treatment with acetic anhydride and concentrated sulphuric acid; small, white needles, m. p. 193—194°.

In the nitration of benzoyl-2 : 3-dinitro-*p*-anisidine another product is formed besides nitrobenzyl-2 : 3 : 6-trinitro-*p*-anisidine. It forms pale yellow needles, and has m. p. 259°. Analysis points to the formula $C_{14}H_{10}O_8N_4$, and it is either a benzoyltrinitroanisidine or a nitrobenzoyldinitroanisidine. T. S. P.

Amines. III. Alkylations with Dimethyl Sulphate. Synthesis of Dimethylphenylethylamine. Treat B. Johnson and Herbert H. Guest (*J. Amer. Chem. Soc.*, 1910, 32, 761—770).—It has been shown previously (Abstr., 1909, i, 785) that methyl iodide reacts with phenylethylamine to form the hydriodide of the original base

* and *Ber.*, 1910, 43, 1849—1853.

and phenylethyltrimethylammonium iodide, but that the mono- and di-methyl derivatives are not produced. It has now been found that phenylethyldimethylamine, $CH_2Ph{\cdot}CH_2{\cdot}NMe_2$, can be prepared by the action of methyl sulphate on phenylethylamine in presence of sodium methoxide. This amine has been obtained in small quantity by Barger (Trans., 1909, **95**, 2195) by heating phenylethyl chloride with dimethylamine. When *p*-nitrophenylethylamine (Johnson and Guest, this vol., i, 311) is treated with methyl sulphate, alkylation does not take place, but the amine remains unchanged. Attempts have also been made to prepare secondary and tertiary amines from *p*-nitrophenylethylamine by alkylation with methyl iodide, but without success.

When methyl sulphate is heated with an ethereal solution of phenylethylamine, *phenylethylammonium methyl sulphate*,

$$CH_2Ph{\cdot}CH_2{\cdot}NH_3{\cdot}SO_4{\cdot}Me,$$

m. p. 75—77°, is obtained in the form of lustrous plates, together with a hygroscopic quaternary *salt*, m. p. 100—110° (decomp.).

Phenylethyldimethylamine, b. p. 200—205°, is a strong base, and absorbs carbon dioxide from the air. The *platinichloride* decomposes at 221°; the *hydrochloride* has m. p. 205°.

When phenylethylmethylamine (Johnson and Guest, *loc. cit.*) is heated with thioacetic acid, *acetyl*-p-*nitrophenylethylmethylamine*, $CH_2Ph{\cdot}CH_2{\cdot}NMeAc$, is obtained as a dark-coloured oil, and, on nitration, yields the p-*nitro*-derivative, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NMeAc$, m. p. 100—101°, which, on oxidation with potassium dichromate, furnishes *p*-nitrobenzoic acid. When acetyl-*p*-nitrophenylethylmethylamine is digested with hydrobromic acid, it is converted into p-*nitrophenylethylmethylamine hydrobromide*; the base was obtained as a heavy, yellow oil. By the action of phenylthiocarbimide on *p*-nitrophenylethylmethylamine, *α-phenyl-β*-p-*nitrophenylethyl-β-methylthiocarbamide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}NHPh$, m. p. 137—138°, is produced, which crystallises in plates.

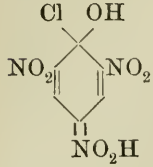
By reducing *p*-nitrophenylethylamine with tin and hydrochloric acid, *p*-aminophenylethylamine (Johnson and Guest, *loc. cit.*) is produced. When *p*-nitrophenylethylamine is heated with methyl iodide, the hydriodide of the amine is obtained, together with p-*nitrophenylethyltrimethylammonium iodide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I$, m. p. 200—201°, which forms hexagonal prisms. E. G.

Solubility Equilibrium between Phenanthrene and 2:4-Dinitrophenol. Robert Kremann and F. Hofmeier (*Monatsh.*, 1910, **31**, 201—202).—Phenanthrene forms additive compounds with trinitrobenzene and trinitrotoluene, but not with the dinitro-compounds (Abstr., 1905, i, 77; 1909, i, 29).

An examination of the freezing-point curve of mixtures of phenanthrene and 2:4-dinitrophenol proves that these compounds do not form a definite compound; the curve has only one eutectic point, namely, at 61°. J. J. S.

Picric Acid. A. Stepanoff (*Annalen*, 1910, **373**, 219—226).—The solubility of picric acid in water is decreased at first by the addition of hydrogen chloride, but reaches a minimum when the solution contains roughly 0·5 millimol. of picric acid and 150 millimols.

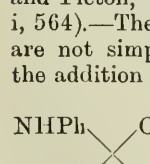
of hydrogen chloride in 100 c.c. of the solution, after which the solubility increases as the concentration of hydrogen chloride becomes greater. It seems probable, therefore, that picric acid and hydrogen chloride combine, forming an unstable additive product having the annexed formula, the proportion of which capable of existing in solution will depend on the concentration of the hydrogen chloride. If the quantity of hydrogen chloride is insufficient, the additive compound will decompose, yielding the true trinitrophenol rather than the *aci*-form, since not only do quinonoid compounds tend to pass into benzenoid compounds, but the true trinitrophenol is less soluble than the coloured *aci*-form.



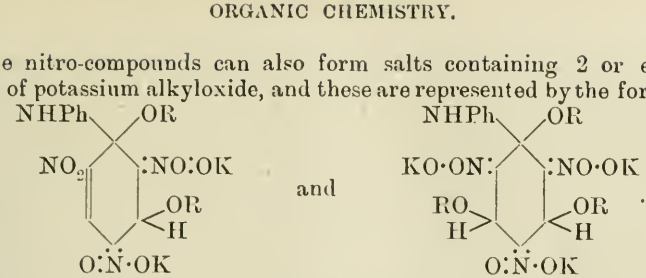
The dark modification of picric acid described by Georgievics (compare Abstr., 1906, i, 420) is shown to be ammonium picrate, formed by the absorption of ammonia from the air. W. H. G.

Colour of Ammonium Picrate. A. Stepanoff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 495—497).—By rapid crystallisation of an almost saturated solution, or by the action of gaseous ammonia on picric acid, a bright yellow ammonium picrate is obtained, the crystals being much smaller than those of the brownish-yellow variety, which is obtained on slower crystallisation; both modifications give a bright yellow powder (compare Silberrad and Phillips, Trans., 1908, **93**, 474). These two forms can be deposited in one and the same vessel by varying the rate of cooling, and show no sign of changing, one into the other, when left in this vessel for some months. Heating for some hours at 100° is likewise unaccompanied by interconversion of the two forms. At 170—180° part of the picrate volatilises, the crystals becoming corroded and assuming a yellow colour. The solutions of the two modifications are identical. The magnitude of the crystals is without influence on their colour, but in the powdered state the red and yellow forms are optically identical. Under the microscope, fragments of the crystals retain their transparency (compare Hantzsch, Abstr., 1906, i, 352, 353; 1907, i, 207, 500; Dimroth and Dienstbach, Abstr., 1909, i, 62; Korczyński, Abstr., 1909, i, 148). T. H. P.

Salts of Aromatic Polynitro-compounds. Max Busch and Walter Kögel (*Ber.*, 1910, **43**, 1549—1564. Compare Sudborough and Picton, Trans., 1906, **89**, 593; Busch and Pungs, Abstr., 1909, i, 564).—The salts formed from compounds of the type of picrylaniline are not simple compounds: $C_6H_2(NO_2)_3\cdot NKPh$, but are formed by the addition of potassium alkyloxide to the nitro-compound, and are represented by quinonoid formulæ, for example, the annexed constitution. Compounds of the type of picrylmethylaniline also yield similar salts, the only exception being picrylmethyl-α-naphthylamine, which appears to be incapable of forming salts. Picryl-α-naphthylamine forms a potassium salt which does not contain alcohol (compare Sudborough and Picton, *loc. cit.*).



The nitro-compounds can also form salts containing 2 or even 3 mols. of potassium alkyloxide, and these are represented by the formulæ:



The di-potassium compounds, as a rule, have not such a deep red colour as the mono-potassium salts, and the tri-potassium salts, which have a hexamethylene constitution, are pale yellow in colour.

Picrylaniline potassium methoxide (*potassium* 3 : 5-*dinitro*-4-*anilino*-4-*methoxyquinolnitrosate*), $C_{13}H_{11}O_7N_4K$, crystallises in glistening, black plates with a steel-blue lustre. It loses a molecule of methyl alcohol when heated at 111°, melts at 115—120°, and explodes at higher temperatures. The corresponding *ethyl* compound has m. p. 115°.

Picrylaniline dipotassium ethoxide, $C_{16}H_{18}O_8N_4K_2$, forms dark red crystals with no definite m. p., and the *tripotassium ethoxide*,

$$C_{18}H_{23}O_9N_4K_3,$$

forms a yellow, microcrystalline powder, which turns red when washed with alcohol.

Picrylaniline potassium propoxide, bluish-black plates, and the corresponding *tripotassium* compound have been prepared. With potassium hydroxide in *iso*butyl alcoholic solution, only the *tripotassium* salt, $C_{24}H_{35}O_9N_4K_3$, could be obtained as an orange-yellow precipitate.

Picrylmethylaniline tripotassium ethoxide is a reddish-brown amorphous powder. *Picrylmethylaniline dipotassium propyloxide*, $C_{19}H_{24}O_8N_4K_2$, is similar.

Picryl-β-naphthylamine potassium methoxide, $C_{17}H_{13}O_7N_4K$, forms black needles, m. p. 173°, and is hydrolysed by water. The corresponding *ethoxide*, $C_{18}H_{15}O_7N_4K$, has m. p. 168°, and the *dipotassium* iso*butyloxide*, $C_{20}H_{18}O_7N_4K_2$, is a pale red, amorphous compound.

Picryl-α-naphthylamine is oxidised in alcoholic solution by an *N*-solution of silver nitrate to an orange-coloured, crystalline *compound*, $C_{16}H_{10}O_7N_4$, m. p. 296—297°.

Picryl chloride and methyl-α-naphthylamine yield an additive *compound*, $C_{17}H_{11}O_6N_4Cl$, in the form of dark red, felted needles, m. p. 94°.

Dibenzylpicramide, $C_{20}H_{16}O_6N_4$, crystallises in yellow needles, m. p. 173°, and yields a potassium salt.

2 : 4-*Dinitrodiphenylamine potassium methoxide*, $C_{13}H_{12}O_5N_3K$, crystallises in violet-black, glistening needles, and the *potassium* iso*butyloxide*, $C_{16}H_{18}O_5N_3K$, is similar.

The alkyl derivatives of 2 : 4-dinitrodiphenylamine, for example,

$$C_6H_3(NO_2)_2\cdot NEtPh,$$

do not yield potassium salts, neither does dimethyl-2 : 4-dinitroaniline. Methyl-2 : 4-dinitroaniline yields an unstable, dark red *potassium* salt.

s-Trinitrobenzene yields a definite *compound* with 3 molecules of potassium propyloxide, $C_{15}H_{24}O_9N_3K_3$, which forms a red powder. *s*-Trinitrotoluene behaves in a similar manner. J. J. S.

Homochromoisomerism. Arthur Hantzsch (*Ber.*, 1910, 43, 1651—1662).—Chromoisomerides are substances which are chemically identical, but optically dissimilar, exhibiting differences in colour and absorption. The author describes a new kind of isomerism called homochromoisomerism. Homochromoisomerides are identical, not only chemically, but also optically, possessing the same colour, absorption, molecular extinction, and molecular refraction, but differ in m. p., solubility, etc. The only instances so far obtained are those of quinoneoximes and nitrated anilines.

[With Joseph Lister.]—Picrylphenylmethylamine,

$$C_6H_2(NO_2)_3\cdot NMePh,$$

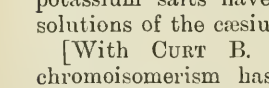
exists in two forms, each of which is unimolecular. The α-form, m. p. 108—110°, has been obtained by Turpin (Trans., 1891, 59, 716), and crystallises unchanged in dark red prisms from methyl or ethyl alcohol, acetic acid, ethyl acetate, ether, acetone, chloroform, carbon tetrachloride, carbon disulphide, and pyridine. The β-form, m. p. 128—129° (Sudborough and Picton, Trans., 1906, 89, 83), crystallises unchanged from benzene, acetonitrile, pyridine, or carbon disulphide. The α-form is converted into the β at 100° or by crystallisation from benzene. The β-form is changed into the α by crystallisation from methyl alcohol, ether, acetone, ethyl acetate, carbon tetrachloride, or chloroform. Both forms have identical absorption spectra, and practically identical molecular extinctions and molecular refractions (in pyridine).

o-Tolyl-2 : 4-dinitroaniline exists in two orange forms (and also in two yellow forms: compare following abstract), which are homochromoisomerides having the same absorption spectra, molecular extinctions, and molecular refractions.

[With R. Flade.]—The *syn*- and the *anti*-modifications of quinoneoximes and also their salts are homochromoisomerides. The two forms of Kehrmann's chlorotoluquinoneoxime have the same absorption spectra and molecular extinctions; the alcoholic solutions of their potassium salts have the same molecular extinctions, and aqueous solutions of the cæsium salts have the same molecular refractions.

[With Curt B. Hartung.]—The preceding instance of homochromoisomerism has led to a more searching examination of the optical behaviour of other stereoisomeric oximes. *syn*- and *anti*-Benzilmonoximes are both colourless, and form yellow alkali salts, but their absorption spectra and molecular extinctions are different. The same is true of the stereoisomeric *p*-nitrobenzaldoximes.

The difference in the optical behaviour of the *syn*- and the *anti*-modifications of benzilmonoxime and also of *p*-nitrobenzaldoxime is probably due to the fact that the oximic hydroxyl is further removed from the unsaturated carbonyl or nitro-group in the *anti*- than in the *syn*-form; in the quinoneoximes the distance is the same in both



modifications, $O{:}C_6H_2MeCl{:}N$ and $O{:}C_6H_2MeCl{:}\dot{N}$, and therefore the

groups exert the same chemical and optical influence in both cases.

Homochromoisomerism, therefore, may represent an extreme case of stereoisomerism in which the mutual influence of unsaturated groups is not markedly affected by differences of configuration. C. S.

Chromoisomerism and Homochromoisomerism of Nitroanilines. Arthur Hantzsch (*Ber.*, 1910, **43**, 1662—1685).—A large number of nitrated anilines have been examined for the existence of differently coloured isomerides (chromoisomerides) or of similarly coloured isomerides (homochromoisomerides). Examples of the latter have been found only in picrophenylmethylamide and in *o*-tolyl-2 : 4-dinitroaniline (preceding abstract), but instances of chromoisomerides are quite numerous in mono-, di-, and tri-nitroanilines containing mono- or di-substituted amino-groups.

The author develops his views at some length in a manner unsuitable for abstraction, and arrives at the following conclusions.

Nitrated anilines can exist in yellow, orange, and dark red forms; occasionally also in modifications having the same colour but different m. p. All these forms are unimolecular in solution. In one and the same solvent isomeric nitroanilines are optically identical, exhibiting the same absorption spectra, molecular refractions, and extinctions. Chromoisomeric nitroanilines contain chromophores of different constitution, whilst the constitutions of homochromoisomerides are explained on stereochemical grounds (preceding abstract). C. S.

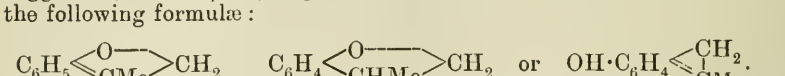
Peculiar Change Caused by Heating Salts of Phenolsulphonic Acids. Julius Obermiller (*Ber.*, 1910, **43**, 1413—1420).—The melting of potassium *o*- and *p*-phenolsulphonates at 255—260° and 325—330° respectively are not cases of true fusion, but are caused by the decomposition of the salts with liberation of phenol. Thus potassium *o*-phenolsulphonate, when heated at a temperature not exceeding 300°, gives off about one-half of its phenol, and leaves an infusible residue consisting of potassium phenol-2 : 4-disulphonate containing a little phenol-2 : 4 : 6-trisulphonate. Other salts, such as the sodium, magnesium, and barium salts, which are infusible, behave in a similar way, only more slowly and at a higher temperature.

C. S.

Structural Conditions Determining Anomalies in Boiling Points Among *o*-Substituted Phenols. C. Guillaumin (*Bull. Soc. chim.*, 1910, [iv], **7**, 426—431).—It is known that phenols containing the group $-CHO$ or $-CO\cdot OR$ in the ortho-position to the hydroxyl show anomalous boiling points; thus, *o*-hydroxybenzaldehyde, b. p. 196°, might be expected to boil at 245° (approx.), and methyl salicylate has b. p. 224°, instead of the expected value, 260°. Similar anomalous boiling points are shown by phenols containing the ψ-allyl side-chain in the ortho-position.

The author correlates these anomalies with (1) the presence of a free hydroxyl group, (2) the existence of an ortho-substituent possessing a double linking to the cyclic atom (carbon or nitrogen). It is possible

that such substances may at the point of ebullition pass into tautomeric forms of lower boiling point, and possible formulæ for these are suggested; thus ψ-allyl-*o*-phenol might be represented by one of the following formulæ:



(I.) (II.) (III.)

No. II has a coumaran nucleus, and probably represents too stable a structure for this purpose. No. I would explain the lowering of boiling points in these compounds, but No. III has the advantage of being more readily applicable to the other cases mentioned, such as salicylaldehyde, methyl salicylate, etc. T. A. H.

Dehydrodicarvacrol. Henri Cousin and Henri Hérissey (*Compt. rend.*, 1910, 150, 1333—1336).—Dehydrodicarvacrol, $OH\cdot C_6H_2MePr^{\beta}\cdot C_6H_2MePr^{\beta}\cdot OH$, was obtained in an impure state by Dianine (Abstr., 1882, 623), and described under the name of β-thymol. It is best prepared as follows: Carvacrol (40 c.c.) is dissolved in 95% alcohol (400 c.c.), and poured into 100 litres of water. The liquid is shaken, filtered, and treated with 300 c.c. of ferric chloride solution (26%). After ten days the precipitate is collected, dissolved in alkali, reprecipitated by acetic acid, and crystallised from dilute alcohol, from which the compound separates in long, silky needles, m. p. 165—166°, containing $2H_2O$.

Dehydrodicarvacrol gives no coloration with ferric chloride. The *dimethyl ether* crystallises in small prisms, m. p. 110°; the *diacetate* forms lamellæ or felted needles, m. p. 182—183°; the *dibenzoate* occurs in long, prismatic needles, m. p. 185°. W. O. W.

Reduction with Metallic Calcium and Absolute Alcohol. Charles Marschalk and Fanny Nicolajewsky (*Ber.*, 1910, 43, 1700—1702. Compare this vol., i, 269).—By means of metallic calcium and absolute alcohol, benzoveratrole, veratroylveratrole, and veratroyl quinol dimethyl ether are reduced to the corresponding leuco-compounds. Tetramethyl-*p*-diaminobenzophenone forms tetramethyl-*p*-diaminobenzhydrol. Naphthalene and anthracene yield dihydro-compounds; quinoline yields tetrahydroquinoline and an amorphous product. Pyridine yields ammonia and small quantities of a base with an odour like piperidine, indicating the opening of the ring; piperidine gives no ammonia. E. F. A.

***cyclo*Hexanetriols and their Derivatives.** Léon Brunel (*Compt. rend.*, 1910, 150, 986—988. Compare Abstr., 1905, *i*, 869).—When an ethereal solution of ethoxy-Δ^2-*cyclo*hexene is treated with iodine and mercuric oxide, an oily liquid is obtained having the composition $OEt\cdot C_6H_9I\cdot OH$, whilst if alcohol is used as the solvent, the composition of the product is represented by $C_6H_9I(OEt)_2$.

Potassium hydroxide converts the first-mentioned iodo-derivative into an *ether*, b. p. 90—91°/25 mm., which, when heated with water, furnishes *ethoxy*cyclo*hexane*-2:3-*diol*, $OEt\cdot C_6H_9(OH)_2$, b. p.

148—149°/20 mm. When this is hydrolysed by aqueous hydrobromic acid, a mixture of triols is obtained, which may be separated by fractional crystallisation of their acetates or benzoates.

α-cyclo*Hexane*-1 : 2 : 3-*triol*, $C_6H_9(OH)_3$, crystallises in needles, m. p. 108°; the *triacetate* forms prisms, m. p. 126° with sublimation; the *tribenzoate* occurs in long needles, m. p. 141—142°. *β*-cyclo*Hexane*-1 : 2 : 3-*triol*, m. p. 124°, forms a syrupy *triacetate* and a *tribenzoate* crystallising in large prisms, m. p. 181°. The *β*-compound is formed in larger proportion and free from the *α*-isomeride by oxidising ethoxy*cyclo*-Δ^2-hexane with alkaline permanganate and treating the product, *ethoxy*cyclo*hexane*-2 : 3-*diol*, with hydrobromic acid. W. O. W.

Phenols of the Type $OH\cdot C_6H_3Me\cdot CMe{:}CH_2$ with *ψ*-Allyl Side-chains. I. *ψ*-Allyl-*o*-cresol. II. *ψ*-Allyl-*m*-cresol. III. *ψ*-Allyl-*p*-cresol. C. Guillaumin (*Bull. Soc. chim.*, 1910, [iv], 7, 374—383).—The synthesis of the methyl ethers of these *ψ*-allyl phenols has been described already (Béhal and Tiffeneau, Abstr., 1908, i, 630, and this vol., i, 374; Guillaumin, this vol., i, 375). In this paper an account is given of the application of analogous methods to the preparation of the three isomeric phenols and their derivatives.

Methyl *o*-hydroxytoluate, D^0 1·1683, $D^{16\cdot8}$ 1·1529, $n_D^{16\cdot8}$ 1·53538, m. p. −0·5°, b. p. 237—239°/760 mm. or 119—121°/14 mm. (corr.), furnishes with magnesium methyl iodide (3·5 mols.) *o-hydroxytolyldimethylcarbinol*, $OH\cdot C_6H_3Me\cdot CMe_2\cdot OH$ [2 : 1 : 3], m. p. 75·5°, b. p. 140—144°/14 mm. (corr.), which forms colourless crystals from benzene, and when heated decomposes at 208—213°, yielding an unsaturated hydrocarbon; when heated with acetic anhydride during twelve hours it furnishes *o-acetoxy-ψ-allyltoluene*,

$$OAc\cdot C_6H_3Me\cdot CMe{:}CH_2$$

[2 : 1 : 3], D^0 1·0337, b. p. 236—238°/760 mm. or 115—116°/13 mm. (corr.), a colourless liquid, which gradually becomes green and decolorises bromine or potassium permanganate. On hydrolysis with potassium hydroxide in alcohol, this acetate furnishes *ψ*-allyl-*o*-cresol, $OH\cdot C_6H_3Me\cdot CMe_2{:}CH_2$ [2 : 1 : 3], D^0 1·0143, $D^{15\cdot6}$ 0·9980, $n_D^{15\cdot6}$ 1·54193 (compare Béhal and Tiffeneau, *loc. cit.*).

The following meta-isomerides of the above substances were prepared from methyl *m*-hydroxytoluate, D^0 1·1621, $D^{15\cdot2}$ 1·1483, $n_D^{15\cdot2}$ 1·53781, b. p. 242—244°/760 mm. (corr.) (compare Abstr., 1908, i, 630). *m*-Hydroxytolyldimethylcarbinol, m. p. 64°, b. p. 140—143°/14 mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 824), with acetic anhydride yields the corresponding m-*acetoxy-ψ-allyltoluene*, D^0 1·0358 $D^{13\cdot8}$ 1·0238, $n_D^{13\cdot8}$ 1·51790, b. p. 122—123°/764 mm. (corr.), a colourless liquid which becomes lemon-yellow after several days. On hydrolysis this acetate yields *ψ*-allyl-*m*-cresol, D^0 1·0241, $D^{14\cdot6}$ 1·0130, $n_D^{14\cdot6}$ 1·55329, b. p. 221—222°/758 mm. or 106—107°/13 mm. (corr.), a colourless liquid giving a green coloration with ferric chloride (compare Fries and Fickewirth, Abstr., 1908, i, 160). It condenses with chloroacetic acid, forming *ψ-allyl*-m-*tolyloxyacetic acid*, m. p. 112°, which crystallises from aqueous alcohol in colourless needles, and polymerises rapidly on distillation at atmospheric pressure.

The following para-isomerides were prepared in like manner from

methyl *p*-hydroxytoluate, D^0 1·1673, $D^{15·8}$ 1·1534, $n_D^{15·8}$ 1·53514, m. p. −1°, b. p. 241—243°/767 mm. or 122—124°/14 mm. (corr.): *p*-Hydroxytolyldimethylcarbinol, m. p. 81°, b. p. 144—148°/14 mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 824). *p-Acetoxy-ψ-allyltoluene*, D^0 1·0383, b. p. 244—246°/763 mm. or 129·5—131·5°/13 mm. (corr.), is a colourless liquid, which becomes orange-red after a few hours. *ψ*-Allyl-*p*-cresol, D^0 1·0285, $D^{15·5}$ 1·0177, $n_D^{15·5}$ 1·54987, b. p. 220—222°/760 mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 160). When condensed with chloroacetic acid, it furnishes *ψ-allyl-p-tolyloxyacetic acid*, $CO_2H·CH_2·O·C_6H_3Me·CMe:CH_2$ [2 : 5 : 1], m. p. 97°, which crystallises in long, colourless needles from boiling alcohol, and is slightly soluble in cold, more so in hot water, and very soluble in ether.

The author was unable to obtain the crystalline polymerides of *ψ*-allyl-*m*-cresol and of its *p*-isomeride described by Fries and Fickewirth (*loc. cit.*). T. A. H.

Phenylic Transposition of *ψ*-Allyl Phenyl Ethers Derived from *o*- or *p*-Cresol. C. Guillaumin (*Bull. Soc. chim.*, 1910, [iv], 7, 420—426).—It has been shown previously that the iodohydrins of aromatic compounds containing *ψ*-allyl side-chains, when treated with silver nitrate or yellow mercuric oxide, are transformed into derivatives of acetone, thus: $Ar·CMe(OH)·CH_2I \longrightarrow Ar·CH_2·COMe$ (Tiffeneau, Abstr., 1907, i, 304; 1908, i, 165, 166). It is now shown that a like transposition is brought about by the action of moist silver oxide on the iodohydrin, but that in this case the iodine atom is, in part, normally replaced by an −OH group, giving rise to the corresponding glycol, thus: $Ar·CMe(OH)·CH_2I \longrightarrow Ar·CMe(OH)·CH_2·OH$. The substances studied so far indicate (1) that "steric hindrance" plays no part in preventing the transposition of the aromatic radicle in the first action, and (2) that in the transposed aromatic radicle no change in the positions of substitution occurs.

2-Methoxy-1-methyl-3-*ψ*-allylbenzene (this vol., i, 375), on treatment with iodine and yellow mercuric oxide in ether, gives an iodohydrin, which with silver nitrate furnishes 2-*methoxy*-1-*methyl*-3-*acetonylbenzene*, D^0 1·0571, b. p. 257—259°/763 mm. (corr.); the sodium hydrogen sulphite compound of this is readily dissociated by water; the *semicarbazone*, recrystallised from benzene, separates into two fractions, m. p. 169° and 171° respectively. With moist silver oxide the iodohydrin yields the same ketone, and in addition the *glycol*,

$$OMe·C_6H_3Me·CMe(OH)·CH_2·OH \text{ [2 : 1 : 3]},$$

b. p. 200—220°/13 mm., D^0 1·1100, a viscous liquid, which on distillation at atmospheric pressure furnishes the corresponding *aldehyde*, $OMe·C_6H_3Me·CHMe·CHO$ [2 : 1 : 3].

4-Methoxy-1-methyl-3-*ψ*-allylbenzene furnishes an iodohydrin, which on treatment with silver nitrate yields 4-*methoxy*-1-*methyl*-3-*acetonylbenzene*, b. p. 266—267°/75 mm. (corr.), D^0 1·0583, $D^{14·8}$ 1·0460, $n_D^{14·8}$ 1·52324, a colourless liquid, which combines with sodium hydrogen sulphite only when pure, and in concentrated solution in ether; the *semicarbazone*, m. p. 150°, crystallises from benzene. T. A. H.

Conversion of Hydroaromatic Alcohols into the Corresponding Phenols. Léon Brunel (*Compt. rend.*, 1910, **150**, 1528—1530).—To ascertain whether the side-chain undergoes any change during the direct hydrogenation of thymol by the method already described (Abstr., 1905, i, 197), the author has oxidised the product, thymomenthol, with chromic acid, and brominated the thymomenthone so formed. *Dibromothymomenthone*, $C_{10}H_{16}OBr_2$, crystallises in large prisms, m. p. 97°, and on heating with quinoline furnishes thymol identical with the starting material. Thymol was also formed on submitting menthol or thymomenthol to catalytic dehydrogenation in presence of reduced copper at 230—240°. Under the same conditions, carvomenthol (Abstr., 1906, i, 81) was converted into carvacrol, an unsaturated *hydrocarbon*, $C_{10}H_{18}$, b. p. 174—176°, being formed as a by-product. The corresponding *hydrocarbon* from menthol or thymomenthol had b. p. 166—168°. W. O. W.

Simple Formation of Benzyl Ethers. Julius von Braun (*Ber.*, 1910, **43**, 1350—1352).—Compounds such as benzyl bromide and *o*-xylyl bromide, when boiled with dilute sulphuric acid and alcohol, or even with dilute alcohol, have the bromine replaced by the alkyloxy-group, and ethers are formed.

In this way the following have been prepared: Benzyl methyl ether, b. p. 174° (previously given as 167—171°); benzyl ethyl ether, b. p. 189° (previously given as 185—186°); *o-xylyl ethyl ether*, b. p. 208—210°, which has an odour like peppermint; *benzyl allyl ether*, b. p. 204—205°, which has a pleasant ethereal odour; at the same time a compound, which is not volatile in steam, b. p. 150—152°/9 mm., is obtained.

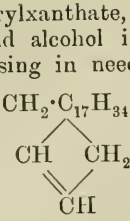
Benzyl bromide also reacts with glycol and glycerol, but a mixture of products is formed. Phenylethyl bromide does not react with alcohol in this manner. E. F. A.

Aminoaryl Alcohols. II. Formation of a Phenylglycol from the Ammonium Base of α-Amino-α-phenyl*iso*propyl Alcohol. Hermann Emde and Ernst Runne (*Ber.*, 1910, **43**, 1727—1729. Compare Abstr., 1909, i, 300).—The quaternary ammonium base derived from α-amino-α-phenyl*iso*propyl alcohol when warmed in aqueous solution is decomposed into trimethylamine and the β-form of α-phenylpropylene αβ-glycol (compare Zincke, Abstr., 1884, 1003; Zincke and Zahn, this vol., i, 316). The quaternary base contains two asymmetric carbon atoms, but fractional crystallisation of the following salts did not lead to any separation of the isomerides.

The *iodide*, $NMe_3I{\cdot}CHPh{\cdot}CHMe{\cdot}OH$, forms hard, short crystals, m. p. 176—177°. The *chloride*, $+H_2O$, crystallises in transparent, long plates, m. p. 138—139°, or when anhydrous, m. p. 196—197°. The *platinichloride* crystallises well, decomp. 233—234°; the *aurichloride* forms long, single needles, m. p. 151·5°, decomp. 220°. E. F. A.

Derivatives of Cholesterol. Leo Tschugaeff and W. Fomin (*Compt. rend.*, 1910, **150**, 1435—1437. Compare this vol., i, 31).—Cholesterylene, previously obtained by the decomposition of methyl

cholesterylxanthate, has now been separated by crystallisation from ether and alcohol into two isomeric hydrocarbons: *α-cholesterylene*, crystallising in needles, m. p. 77°, $[\alpha]_D$ −109·3° in toluene, and *β-cholesterylene*, m. p. 59°, $[\alpha]_D$ −76·68°, in toluene solution. Both compounds show normal rotatory dispersion. When treated with hydrogen in presence of platinum-black, they yield the same hydrocarbon, cholestane, identical with that obtained from cholestene by Mauthner (Abstr., 1909, i, 714).



The annexed constitution is suggested for cholesterylene, the two modifications being supposed to differ in the position of the double linking in the ring. W. O. W.

Interchange of Alkyl Groups in Esters of Organic Acids. Michael Pfannl (*Monatsh.*, 1910, 31, 301—317).—It has long been known that the alkyl group of an ester can be exchanged for another alkyl group by means of sodium or an alkali hydroxide dissolved in the alcohol corresponding with the second alkyl group. By means of experiments on the methyl, ethyl, and propyl esters of terephthalic acid, of benzoic acid, and of oxalic acid, the author shows that the exchange is quite general, and is completely reversible. The method consists in dissolving a known quantity of an ester in at least ten times the amount of an alcohol, and adding in the cold a quantity of potassium hydroxide or of sodium dissolved in the alcohol in question; the exchange proceeds to completion at the ordinary temperature in a time, thirty minutes to fifteen hours, depending on the amount of alkali present, the greater the amount of alkali the shorter the time required; the alkali is then neutralised, water is added, and the new ester is removed by ether or by filtration.

The velocity of the exchange is directly proportional to the quantity of alkali present; consequently Kremann's theory that the alkali acts merely as a catalyst (Abstr., 1908, i, 120) must be incorrect. The author regards Claisen's explanation:

$$CPh\langle{O \atop OR} + KOR' = CPh\langle{OR' \atop OK \atop OR} \longrightarrow CPh\langle{OR' \atop O} + KOR$$

as affording the best interpretation of the results, for it explains (i) the reversibility of the exchange, (ii) the absence of any exchange in the absence of alkali, (iii) the absence of any exchange in the case of substances, such as phenolic ethers, which are unable to add on potassium alkyl oxide, (iv) the proportionality between the velocity of the exchange and the concentration of the alkali. C. S.

*cyclo*Hexylglycollic Acid. Marcel Godchot and Jules Frezouls (*Compt. rend.*, 1910, 150, 1248—1250. Compare Zelinsky and Schwedoff, Abstr., 1908, i, 864).—*cyclo*Hexylglycollonitrile undergoes decomposition when distilled; hydrochloric acid converts it into the *amide*, crystallising in pearly leaflets, m. p. 155°. The free acid obtained by the hydrolysis of the amide with alkalis occurs as

prismatic needles, m. p. 130—131°; the *sodium* and *silver* salts have been analysed. In the authors' opinion, the acid described under this name by Zelinsky and Schwedoff was a mixture. W. O. W.

[Preparation of Isomeric Nitrobenzoyl Derivatives of Nitroanilines, Nitrotoluidines, and their Reduction Products.] Gesellschaft für Chemische Industrie in Basel (D.R.-P. 221433).—An account of the preparation of dyes from tetrazotised compounds of the general formula $NH_2 \cdot R \cdot NH \cdot CO \cdot C_6H_4 \cdot NH_2$ (R = an aromatic nucleus) combined with two molecules of various naphtholsulphonic acids.

The following initial compounds are mentioned, and were prepared by the usual methods: m-*Nitrobenzoyl*-p-*nitroaniline*, yellow powder, m. p. 249°. m-*Aminobenzoyl*-p-*phenylenediamine*, brown needles, m. p. 150°. p-*Nitrobenzoyl*-p-*nitroaniline*, yellow, crystalline powder, m. p. 266°. p-*Aminobenzoyl*-p-*phenylenediamine*, brown needles, m. p. 205°, soluble in hot water. m-*Nitrobenzoyl*-m-*nitroaniline*, brown needles, m. p. 185°. m-*Aminobenzoyl*-m-*phenylenediamine*, m. p. 130°. p-*Nitrobenzoyl*-m-*nitroaniline*, yellow needles, m. p. 227°. p-*Aminobenzoyl*-m-*phenylenediamine*, grey powder, m. p. 173°. m-*Nitrobenzoyl*-p-*nitro*-o-*toluidine*, colourless, glistening leaflets, m. p. 193°. m-*Aminobenzoyl*-m-*tolylenediamine*, brown, crystalline powder, m. p. 177°. p-*Nitrobenzoyl*-p-*nitro*-o-*toluidine*, brownish-yellow needles, m. p. 214°.

F. M. G. M.

Bromination of Anthranilic Acid. Alvin S. Wheeler and W. M. Oates (*J. Amer. Chem. Soc.*, 1910, **32**, 770—773).—A study has been made of the action of bromine on anthranilic acid dissolved in glacial acetic acid, both near the m. p. of the acetic acid and also near its b. p. In the former case the product consists of 5-bromo-2-aminobenzoic and 3 : 5-dibromo-2-aminobenzoic acids in the proportion of 2 : 1, whilst in the latter case the proportions are almost exactly reversed.

The *silver* salt and *ethyl* ester, m. p. 187°, of 5-bromo-2-aminobenzoic acid are described. 5-Bromoacetylanthranil has m. p. 134° (compare Bogert and Hand, Abstr., 1906, i, 176). 3 : 5-*Dibromoacetylanthranil*, m. p. 176°, forms long, colourless needles. 3 : 5-*Dibromoacetyl*-2-*aminobenzoic acid*, m. p. 218—219°, obtained by boiling the anil with dilute sodium hydroxide or with glacial acetic acid, crystallises in microscopic needles; its *silver* salt decomposes at about 270°, and its *ethyl* ester has m. p. 74°. E. G.

Esterification. Esterification of Thiolbenzoic Acid by Alcohol and of Benzoic Acid by Mercaptan. E. Emmet Reid (*Amer. Chem. J.*, 1910, **43**, 489—504).—In accordance with Henry's hypothesis, the esterification of thiolbenzoic acid by alcohol should take place as follows: $C_6H_5 \cdot CO \cdot SH + EtOH \rightleftharpoons C_6H_5 \cdot C(OH)(SH) \cdot OEt$, and this additive compound may break up into $C_6H_5 \cdot CO_2Et + H_2S$ or into $C_6H_5 \cdot CS \cdot OEt + H_2O$. In the esterification of benzoic acid by mercaptan, the reaction would be in accordance with the equation: $C_6H_5 \cdot CO_2H + EtSH \rightleftharpoons C_6H_5 \cdot C(OH)_2 \cdot SEt \rightleftharpoons C_6H_5 \cdot CO \cdot SEt + H_2O$.

Qualitative and quantitative experiments have been carried out in order to study these reactions, and to ascertain the mode and extent of esterification of mercaptan.

It has been found that when hydrogen chloride is passed into a solution of thiolbenzoic acid in alcohol, hydrogen sulphide and ethyl benzoate are produced, but ethyl thionbenzoate does not seem to be formed. The reaction proceeds according to the equation :

$$C_6H_5\cdot CO\cdot SH + EtOH = C_6H_5\cdot CO_2Et + H_2S.$$

The same change takes place in the absence of a catalytic agent when thiolbenzoic acid and alcohol are heated in a sealed tube at about 150°. The reaction is not reversible. Thiolbenzoic acid is not produced by the action of hydrogen sulphide on ethyl benzoate, but benzoic acid and mercaptan are obtained thus: $C_6H_5\cdot CO_2Et + H_2S = C_6H_5\cdot CO_2H + EtSH$.

Mercaptan has the power of forming esters, both in presence and absence of a catalytic agent, but is less efficient than alcohol. The reaction between benzoic acid and mercaptan is reversible, and is expressed by the equation : $C_6H_5\cdot CO_2H + EtSH = C_6H_5\cdot CO\cdot SEt + H_2O$. It obeys the law of mass action, and a true equilibrium is reached with about 16·8 per cent. of esterification. E. G.

Synthesis of Aromatic Nitriles. F. Bodroux and Felix Taboury (*Compt. rend.*, 1910, 150, 1241—1243. Compare this vol., i, 257).—Nitriles of the type CHPhR·CN condense with alkyl halides in the presence of sodamide, giving nitriles of the type CPhRR'·CN. The following compounds have been prepared in this way : *α-phenyl-α-ethylbutyronitrile*, $CEt_2Ph\cdot CN$, b. p. 125·5—127°/13 mm., 247—249°/752 mm., $D^{16\cdot5}$ 0·957 ; *α-phenyl-γ-methyl-α-isopropylvaleronitrile*, $CH_2Pr^{\beta}\cdot CPr^{\beta}Ph\cdot CN$, b. p. 148—150°/15 mm., D^{16} 0·932. Similar compounds have also been prepared by the direct action of alkyl halides on phenylacetonitrile in presence of sodamide; thus *n*-propyl bromide furnishes *α-phenyl-α-n-propylvaleronitrile*, $CPr^{\alpha}_2Ph\cdot CN$, b. p. 142·5—145°/15 mm., 268—270°/758 mm., D^{14} 0·940 ; *iso*butyl bromide yields *α-phenyl-γ-methyl-α-isobutylvaleronitrile*, $C(CH_2Pr^{\beta})_2Ph\cdot CN$, b. p. 152—155°/15 mm., D^{13} 0·931. W. O. W.

Compounds of 3 : 5-Dinitro-4-hydroxybenzoic Acid with Hydrocarbons. Otto Morgenstern (*Monatsh.*, 1910, 31, 285—294). —3 : 5-Dinitro-4-hydroxybenzoic acid, the ammonium salt of which exists in a yellow and a red modification, resembles picric acid in forming coloured compounds with aromatic hydrocarbons The following *compounds* are described : with acenaphthene,

$$C_{12}H_{10},C_7H_4O_7N_2,$$

m. p. 210—211° (decomp.), reddish-orange needles ; with naphthalene, $C_{10}H_8,C_7H_4O_7N_2$, m. p. 214—217° (in closed tube), yellow needles ; with pyrene, $C_{16}H_{10},C_7H_4O_7N_2$, m. p. 251—252° (decomp.), orange-red needles ; with fluorene, $C_{13}H_{10},2C_7H_4O_7N_2$, m. p. 218—221°, pale yellow powder ; with retene, $C_{18}H_{18},2C_7H_4O_7N_2$, pale yellow leaflets decomposing at 229—231° ; with diphenylene oxide,

$$C_{12}H_8O,2C_7H_4O_7N_2,$$

m. p. 226—232° (decomp.), pale yellow needles; with phenanthrene, $C_{14}H_{10},2C_7H_4O_7N_2$, m. p. 218—222°, reddish-yellow needles; with quinoline, $C_9NH_7,C_7H_4O_7N_2$, citron-yellow powder decomposing at 224·5—225°.

All these compounds are prepared by mixing alcoholic solutions of the constituents and subsequently concentrating the mixture, if necessary; they are more or less unstable, and are partly decomposed by recrystallisation from alcohol, and completely by benzene at the ordinary temperature. C. S.

Lactonoid Anhydrides of Acylated Amino-acids. III. The Lactone of *r*-Benzoylalanine and its Application for the Synthesis of Benzoylated Dipeptides. Ernst Mohr [with Fr. Stroschein] (*J. pr. Chem.*, 1910, [ii], 81, 473—500. Compare this vol., i, 116, 117).—The *lactone*, $CHMe<^{N=CPh}_{CO\cdot O}$, m. p. 39—39·5°, of *r*-benzoylalanine is obtained by heating finely powdered benzoylalanine and acetic anhydride on the water-bath for not more than ten minutes, removing the acetic acid formed and the excess of the anhydride under 0·2—0·5 mm. pressure, and finally distilling the lactone, which passes over at 75—140°/0·2—0·5 mm., and crystallises by keeping in a vacuum desiccator. The lactone develops a temporary intense bluish-violet fluorescence by treatment with *N*/10-sodium hydroxide, and in its chemical behaviour resembles the lactone of benzoyl-*a*-amino*iso*butyric acid. It easily yields benzoylalanine with hot water, benzoylalanineamide with ethereal ammonia, ethyl benzoylalanine with alcohol, benzoylalanyl chloride with cold ethereal hydrogen chloride, and Curtius and van der Linden's benzoylalanineanilide with ethereal aniline. Whether prepared in this way or from ethyl benzoylalanine and aniline, or from benzoylalanyl chloride and aniline, the anilide has m. p. 176—176·5°, not 163—165° as given by these authors (Abstr., 1904, i, 883).

Curtius and van der Linden's benzoylalanylglycine (*loc. cit.*) is obtained by adding the lactone to aqueous glycine, keeping the mixture faintly alkaline during the reaction, and subsequently acidifying with 10*N*-hydrochloric acid. In a similar manner, benzoylalanylalanine is obtained from *r*-alanine, and *benzoylalanyl-a-amino*isobutyric acid, $NHBz\cdot CHMe\cdot CO\cdot NH\cdot CMe_2\cdot CO_2H$, m. p. 199—199·5°, from *a*-amino-*iso*butyric acid. By heating with acetic anhydride, the last benzoylated dipeptide alone yields a *lactone*, $NHBz\cdot CHMe\cdot C<^{N\cdot CMe_2}_{O-CO}$, m. p. 116—117°, which reacts with ethereal ammonia at 0° to form *benzoylalanyl-a-amino*isobutyramide, m. p. 209°.

A comparison is drawn between the properties of benzoyl-*a*-amino-*iso*butyric acid, benzoylalanine, and hippuric acid. The last stands somewhat apart from the first two, being most easily decomposed, but the amide of the first yields a cyclic imide with boiling dilute sodium hydroxide, whilst the amides of the second and the last undergo normal hydrolysis. C. S.

Reaction between Unsaturated Compounds and Organic Zinc Compounds. Elmer P. Kohler and Gertrude L. Heritage (*Amer. Chem. J.*, 1910, 43, 475—489).—It has been stated by Kohler and Burnley (this vol., i, 391) that the relation between the character of organic magnesium compounds and their mode of addition to ketones containing the chain C:C·C:O is not easily determined. The results of earlier work show that magnesium compounds containing alkyl groups behave differently from those derived from aromatic compounds which have the halogen directly attached to the nucleus. The former give almost the same amount of the 1 : 4-additive product with any one ketone, whilst magnesium phenyl bromide and magnesium tolyl bromide give relatively a much larger quantity of the 1 : 2-additive product. Attempts have been made to find an explanation for this difference. Owing to certain difficulties which arose, it was decided to substitute zinc for magnesium, and experiments are now described on the action of methyl bromoacetate and zinc on benzylideneacetophenone, benzylidenepropiophenone, and other unsaturated compounds. These ketones give only saturated compounds with the ordinary Grignard reagents, but have been found to yield unsaturated β-hydroxy-esters when they react with zinc and methyl bromoacetate. It has been proved that this difference does not depend on the metal, solvent, or procedure, but is due entirely to the nature of the halogen compounds used.

When a solution of benzylideneacetophenone in benzene is heated with methyl bromoacetate and a slight excess of zinc, 1 : 2-addition takes place with formation of *methyl β-hydroxy-β-phenyl-γ-benzylidenebutyrate*, $CHPh:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me$, m. p. 126°, which crystallises in slender needles. This ester combines with bromine to form a solid *dibromide*, which on recrystallisation from chloroform is converted into *methyl β-hydroxy-β-phenyl-γ-bromobenzylidenebutyrate*, $CPhBr:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me$, which forms thick needles, and begins to decompose at about 200°. Magnesium can be used instead of zinc in the reaction between benzylideneacetophenone and methyl bromoacetate, and, in this case, as in the former, only the 1 : 2-additive compound is produced. When magnesium is employed, ether can be used instead of benzene as a solvent, but the manipulation is troublesome and the yield unsatisfactory.

Methyl β-hydroxy-β-phenyl-γ-benzylidenevalerate,

$$CHPh:CMe\cdot CPh(OH)\cdot CH_2\cdot CO_2Me,$$

m. p. 70°, obtained by the action of methyl bromoacetate on benzylidenepropiophenone in presence of zinc and benzene, or magnesium and ether, forms large, lustrous plates.

When ethylideneacetophenone is treated with methyl bromoacetate and zinc, *methyl β-hydroxy-β-phenyl-Δγ-hexenoate*,

$$CHMe:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me,$$

m. p. 58°, is produced, which crystallises in long needles; its *bromo*-derivative, $CMeBr:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me$, m. p. about 175° (decomp.), forms small prisms or plates.

Cinnamaldehyde, when treated in the same way, gives a product which does not solidify, but, on distillation under reduced pressure, loses water and yields methyl cinnamylideneacetate. This aldehyde

reacts similarly with methyl α-bromopropionate to form methyl α-methylcinnamylideneacetate.

Ethyl β-hydroxy-β-methyl-γ-benzylidenebutyrate, $CHPh{:}CH{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Et$, b. p. 192°/20 mm., obtained from styryl methyl ketone and ethyl bromoacetate, is a colourless liquid, and on hydrolysis with potassium hydroxide yields phenylmethylbutadiene, m. p. 37°. When this ester is boiled with hydrochloric acid, it is converted into *β-methylcinnamylideneacetic acid*, $CHPh{:}CH{\cdot}CMe{:}CH{\cdot}CO_2H$, m. p. 153°, which forms small prisms or plates.

The product obtained from benzylidenepinacolin and methyl bromoacetate loses water on distillation under reduced pressure, and yields *methyl β-butylcinnamylideneacetate*, b. p. 210°/20 mm.

Methyl γ-bromo-β-hydroxy-β-phenyl-γ-benzylidenebutyrate, $CHPh{:}CBr{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2Me$, m. p. 79—80°, prepared from α-bromobenzylideneacetophenone and methyl bromoacetate, forms colourless needles.

Cinnamylideneacetophenone reacts with methyl bromoacetate to form *methyl β-hydroxy-β-phenyl-γ-cinnamylidenebutyrate*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2Me$, m. p. 112°, which crystallises in slender needles.

Benzylidenedeoxybenzoin and benzylideneacetylmesitylene do not react with methyl bromoacetate in presence of zinc, although they readily give 1 : 4-additive compounds with Grignard reagents.

E. G.

Preparation of Iodoacylsalicylic (*o*-Iodoacyloxybenzoic) Acids. Chemische Fabrik von Friedr. Heyden (D.R.-P. 221384).—The *o*-bromoacyloxybenzoic acids have been previously described (Abstr., 1909, i, 798); it is now found that *o*-iodoacyloxybenzoic acids can be readily prepared by similar methods, and are of therapeutic value as antirheumatics.

o-Iodoacetoxybenzoic acid, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2I$, obtained by the interaction of iodoacetyl chloride and sodium salicylate in dry benzene solution, forms colourless needles, m. p. 138° (decomp.).

o-α-Iodoisovaleryloxybenzoic acid, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CHI{\cdot}CHMe_2$, colourless crystals, m. p. 102°, is analogously prepared.

F. M. G. M

Piperonylic Acid. E. Oertly and Amé Pictet (*Ber.*, 1910, **43**, 1336—1340).—*Methyl piperonylate*, $CH_2O_2{:}C_6H_3{\cdot}CO_2Me$, forms colourless needles, m. p. 53°. The *mononitro*-derivative, obtained by interaction with fuming nitric acid and acetic acid, crystallises in colourless needles, m. p. 102°, and on reduction by means of tin chloride and acetic acid is converted into *methyl aminopiperonylate*, which separates in silver-grey needles, m. p. 108°. On replacing the amino-group by carboxyl, hydrastic acid is obtained, showing the amino-group to be in position 6.

Methyl cyanopiperonylate is prepared by diazotising the amino-compound in hydrochloric acid solution and adding potassium cyanide, and crystallises in light yellow needles, m. p. 135—136°. Hydrolysis con-

verts this into hydrastic acid, and this affords a convenient process for preparing this acid. Nitration of methyl hydrastate gives the nitro-compound already described.

The position of the bromine atom in bromopiperonal and bromopiperonylic acid (Fittig and Mielch, *Annalen*, 1869, **152**, 49) was unknown previously. The latter compound yields a *methyl* ester separating in colourless crystals, m. p. 87—88°, which substance is also obtainable from methyl aminopiperonylate by diazotisation and decomposition with copper bromide. This fixes position 6 as that of the bromine atom.

Bromonitrocatechol methylene ether, $CH_2O_2{:}C_6H_2(NO_2)Br$, crystallises in yellow needles, m. p. 87°.

Methyl bromonitropiperonylate, $CH_2O_2{:}C_6H(NO_2)Br{\cdot}CO_2Me$, forms yellow needles, m. p. 131°, and on reduction with ammonium sulphide is converted into *methyl bromoaminopiperonylate*, which separates in greyish-white needles, m. p. 92°. E. F. A.

Synthetical Experiments with *o*-Xylylene Cyanide. Oscar Hinsberg (*Ber.*, 1910, **43**, 1360—1363).—*o*-Xylylene cyanide contains two reactive methylene groups, and therefore condenses in presence of sodium ethoxide with *o*-diketones, keto-acids, and esters of oxalic acids to naphthalene derivatives.

With ethyl oxalate, 1 : 4-*dicyano*-2 : 3-*dihydroxynaphthalene* is formed; this crystallises in a voluminous mass of light yellow plates, m. p. 291°, and shows an intense blue coloration with ferric chloride.

With benzil, 1-*cyano*-2 : 3-*diphenylnaphthalene*-4-*carboxylamide*,

$$C_6H_4\begin{cases}C(CN)=\!=\!=CPh\\ C(CO{\cdot}NH_2){:}CPh'\end{cases}$$

is formed; this separates in colourless crystals, m. p. above 290°.

With phenanthraquinone, *cyanonaphthaphenanthrenecarboxylamide* is obtained, crystallising in minute, yellow needles, m. p. 306°. Hydrolysis of these substances to the corresponding carboxylic acids does not take place easily. E. F. A.

Preparation of Alkyl- and Aryl-oxyacylsalicylic [*o*-Aryloxyacyloxybenzoic] Acids. Chemische Fabrik von Friedr. Heyden (D.R.-P. 221385).—The *o*-alkyl- and *o*-aryl-oxyacylbenzoic acids are prepared by the action of the anhydrides, or alkyl- or aryloxyparaffin acid chlorides on salicylic acid in the presence or absence of condensing agents.

o-Phenoxyacetyloxybenzoic acid, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}OPh$, tasteless, colourless needles, m. p. 143°, is prepared by slowly adding phenoxyacetyl chloride to a suspension of sodium salicylate in benzene at 16° with continual stirring during seven hours.

o-Ethoxyacetyloxybenzoic acid, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}OEt$, colourless needles, m. p. 91°, is analogously prepared from ethoxyacetyl chloride in the presence of dimethylaniline; it has an acid taste, but compares favourably with acetylsalicylic acid in its therapeutic action. F. M. G. M.

Condensation of Ethyl Oxalate with Ethyl Tricarballylate. Henri Gault (*Compt. rend.*, 1910, 150, 1341—1343).—In presence of sodium ethoxide, ethyl oxalate condenses with ethyl tricarballylate to form a mixture of ethyl oxalotricarballylate and ethyl *cyclo*pentandione-1 : 2 : 3-tricarboxylate. Wislicenus (Abstr., 1896, i, 604) gives m. p. 123° for the latter compound, and states that he was unable to effect hydrolysis by acids or alkalis. The present author gives m. p. 127°, and finds that hydrolysis with hydrochloric acid leads to the formation in the first place of *ethyl* cyclo*pentandione*-1 : 2-*dicarboxylate*, $\begin{matrix}CO\text{———}CO\\ |\quad\quad\quad|\\ CH_2\cdot CH(CO_2H)\end{matrix}>CH\cdot CO_2Et$. This substance has m. p. 137°, and develops a reddish-violet coloration with ferric chloride; it forms a *disemicarbazone* and a *diphenylhydrazone*, m. p. 190° (decomp.). Prolonged hydrolysis of the triethyl ester results in the formation of cyclo*pentandionecarboxylic acid*, $\begin{matrix}HO\cdot C=CH\\ |\quad\quad|\\ CO\text{—}CH\end{matrix}>CH\cdot CO_2H$. This has m. p. 137°, gives a red coloration with ferric chloride, and forms a hygroscopic *disemicarbazone* and a *diphenylhydrazone* having m. p. 220° (decomp.). W. O. W.

Action of Alcoholic Ammonia on Acetyltannin and Triacetylgallic Acid. Maximilian Nierenstein (*Ber.*, 1910, 43, 1688—1690).—By the action of alcoholic ammonia on acetyltannin at the ordinary temperature, a mixture of products is formed; at the temperature of the water-bath, gallic acid and gallamide are obtained with other products.

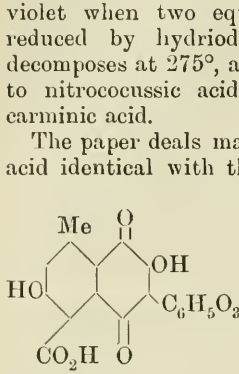
Triacetylgallic acid, when treated with 3 mols. of alcoholic ammonia in the cold, forms *diacetylgallic acid*, crystallising in tiny needles, m. p. 174—176°; this gives a dark green coloration with ferric chloride, and a red coloration with potassium cyanide. It is suggested that the *p*-acetyl group is the one eliminated. E. F. A.

Schiff's Digallic Acid or Artificial Tannin. Pietro Biginelli (*Ber.*, 1910, 43, 1541—1543).—A reply to Nierenstein (this vol., i, 265). The author maintains that Schiff's digallic acid contains an arsenic compound (compare Biginelli, Abstr., 1909, i, 801). The reason why Nierenstein could not detect arsenic was that he did not destroy the organic matter. J. J. S.

Dye of Kermes. Otto Dimroth (*Ber.*, 1910, 43, 1387—1401).—*Kermesic acid*, $C_{18}H_{12}O_9$, the name given by the author to the dye isolated by a slightly modified form of Heise's process from kermes (*Coccus ilicis*), is very similar to carminic acid in tinctorial properties and in its absorption spectrum, but differs from it by its solubility in ether, a property which suggests that the molecule of kermesic acid is smaller than that of carminic acid, and contains fewer hydroxyl groups. Kermesic acid crystallises in brick-red needles, darkens at 250° without melting, and dissolves without decomposition in concentrated sulphuric acid, forming a violet-red solution, the absorption spectrum of which is very similar to that of carminic acid, and both spectra experience the same change by the addition of boric acid.

Kermesic acid is a monocarboxylic acid, which forms a tetra-acetyl *derivative*, $C_{18}H_8O_9Ac_4$, m. p. 245°, and does not contain methoxyl groups. The *disodium* and the *barium* salts are described. The red colour of a dilute alcoholic solution of the acid remains unchanged by the addition of one equivalent of potassium hydroxide, and becomes violet when two equivalents have been introduced. The acid is reduced by hydriodic acid to a red *substance*, $C_{18}H_{12}O_8$, which decomposes at 275°, and is oxidised by warm concentrated nitric acid to nitrococussic acid, the longest known degradation product of carminic acid.

The paper deals mainly with the degradation products of kermesic acid identical with those of carminic acid; an examination of these products leads the author to suggest the annexed formula for kermesic acid, similar to that of carminic acid. Several methylated derivatives can be obtained from kermesic acid. *Kermesic acid trimethyl ether*, $C_{21}H_{18}O_9$, m. p. 310°, is obtained by boiling a suspension of potassium kermesate in toluene with methyl sulphate, digesting the crystalline product with potassium carbonate, and decomposing the insoluble portion with warm dilute hydrochloric acid; the ether is finally crystallised from glacial acetic acid, from which it separates in orange-red needles. Its oxidation by hot potassium permanganate leads to the formation of two acids. One is *methyl cochenillate methyl ether*,



$$OMe\cdot C_6HMe(CO_2H)_2\cdot CO_2Me,$$

which yields an *anhydride*, m. p. 149°, at its m. p., 178—180°, and is hydrolysed by 25% potassium hydroxide to *cochenillic acid methyl ether*, $C_{11}H_{10}O_7$, m. p. 200° (decomp.); both ester and acid are converted into hydroxyuvitic acid by hydriodic acid, D 2·0. The other acid is a *methyl* ester of cresotinglyoxyldicarboxylic acid methyl ether,

$$OMe\cdot C_6HMe(CO_2H)(CO_2Me)\cdot CO\cdot CO_2H,$$

m. p. 108—110° (the hydrated acid has m. p. 86°), which forms a *phenylhydrazone*, m. p. 183°, and is oxidised by sodium carbonate and potassium permanganate to methyl cochenillate methyl ether.

[With Hamburger.]—The last-mentioned compound is obtained, together with cochenillic acid methyl ether, when methyl carminate methyl ether is heated on the water-bath with nitric acid. C. S.

Influence of Ortho-substituents on the Formation of Aldehyde Diacetates. Ernst Späth (*Monatsh.*, 1910, 31, 191—194. Compare Wegscheider and Späth, this vol., i, 155).—Fischer and Giebe (Abstr., 1898, i, 311) have shown that ortho-substituents in an aldehyde facilitate the formation of acetals, with the single exception of *s*-trimethylbenzaldehyde. The author finds that the negative nitro-groups in 2 : 4 : 6-trinitrobenzaldehyde (Sachs and Everding, Abstr., 1902, i, 377) retard the formation of a diacetate from the aldehyde, acetic anhydride, and two drops of sulphuric acid. A better yield of the *diacetate*, $C_6H_2(NO_2)_3\cdot CH(OAc)_2$, is obtained when the mixture is kept for fifteen hours; it crystallises in needles, m. p. 117—118°.

J. J. S.

Chemical Action of Light. XVIII. Giacomo L. Ciamician and Paul Silber (*Ber.*, 1910, **43**, 1536—1541; *Atti R. Accad Lincei*, 1910, [v], **19**, i, 645—650. Compare Abstr., 1901, i, 36; 1903, i, 562).—Solutions of benzophenone in aromatic hydrocarbons undergo change when exposed to light in tubes for some months. In all cases benzopinacone is formed, and the hydrocarbon undergoes condensation. With a solution in cymene, a dicymyl, probably identical with Cannizzaro and Rossi's (*Annalen*, 1862, 121, 251), is formed. With a toluene solution the products are benzopinacone, Cannizzaro and Rossi's dibenzyl, m. p. 52°, and diphenylbenzylcarbinol (Hell and Wiegandt, Abstr., 1904, i, 490), which is formed by the addition of a molecule of toluene to one of benzophenone.

Benzophenone and ethylbenzene yield benzopinacone, the hydrocarbon, $C_{16}H_{18}$, m. p. 124° (Paterno and Chieffi, this vol., i, 42), and the additive product, $C_{21}H_{20}O$, which forms large, monoclinic crystals

$$[a : b : c = 1{\cdot}8207 : 1 : 0{\cdot}6671 ; \beta = 86°11'].$$

When heated at 300° this compound is partly converted into benzophenone and ethylbenzene, but is also partly decomposed into water and a *hydrocarbon*, $C_{21}H_{18}$, m. p. 88°.

Benzophenone and *p*-xylene give benzopinacone, *pp'*-dimethyldibenzyl, and the additive compound, $OH{\cdot}CPh_2{\cdot}CH_2{\cdot}C_6H_4Me$, *diphenyl*-p-*methylbenzylcarbinol*, m. p. 113°, b. p. 258—260°/24 mm.

A mixture of toluene and acetone yields dibenzyl. J. J. S.

Ketonic Derivatives of Benzoic and Phenylacetic Acids. Jean B. Senderens (*Compt. rend.*, 1910, **150**, 1336—1338. Compare Abstr., 1909, i, 286, 627; this vol., i, 11, 179, 318).—The catalytic method already described is advantageous for the preparation of the undermentioned ketones in a state of purity. The corresponding oximes and semicarbazones are best prepared by heating a solution of the ketone in 85% alcohol with pure sodium aluminate and the hydrochloride of hydroxylamine or semicarbazide. Acetophenone; propiophenone, hitherto described as a liquid, crystallises in lamellæ, m. p. 14·5°, b. p. 215°/746 mm. (corr.), D_4^{16} 1·008; phenyl *n*-propyl ketone, m. p. 8·5°, b. p. 229°/746 mm. (corr.), D_4^0 1·001; phenyl *iso*propyl ketone, b. p. 220°/746 mm., D_4^0 0·999; phenyl *iso*butyl ketone, b. p. 236·5°/746 mm. (corr.), D_4^0 0·985, the oxime has m. p. 64·5.

Dibenzyl ketone is obtained in theoretical yield by passing the vapour of phenylacetic acid over thorium oxide at 430°; the *phenylhydrazone* has m. p. 121°; the *semicarbazone*, m. p. 123°. Phenyl benzyl ketone, D_4^0 1·019, gave a *semicarbazone*, decomposing at 165—180°; α-phenylbutan-β-one, b. p. 230°/755 mm. (corr.), D_4^0 1·002, gave a *semicarbazone*, m. p. 135·5° (decomp.); *α-phenylpentan-β-one*, b. p. 244°/760 mm., D_4^0 0·984, the *semicarbazone* has m. p. 82°; *α-phenyl-γ-methylbutan-β-one*, b. p. 237°/760 mm. (corr.), D_4^0 0·985, the *semicarbazone* has m. p. 126°; *α-phenyl-δ-methylpentan-β-one*,

$$CH_2Ph{\cdot}CO{\cdot}CH_2Pr^{\beta},$$

b. p. 250·5°/760 mm. (corr.), D_4^0 0·969, gave a *semicarbazone*, m. p. 80°, and a *phenylhydrazone*, crystallising in yellow needles, m. p. 67°.

W. O. W.

Duplobenzylidenethioacetone; a Correction. Emil Fromm (*Ber.*, 1910, **43**, 1759. Compare Abstr., 1907, i, 710).—The so-called duplobenzylidenethioacetone is a mixture of a non-basic substance and one or more basic compounds which form salts with mineral acids. It is now found that these compounds contain about 4% of nitrogen, which explains their basic properties, and renders the explanation given formerly (*loc. cit.*) quite unnecessary. E. F. A.

Preparation and Properties of 2:2-Dialkyl-1-hydrindones or 2:2-Dialkyl-1-indanones. Albin Haller and Edmond Bauer (*Compt. rend.*, 1910, **150**, 1472—1478. Compare Kipping, Trans., 1894, **65**, 480, Proc., 1901, **17**, 181; Haller and Bauer, Abstr., 1909, i, 109, 655).—Alkylation of 1-hydrindone by means of an alkyl halide in presence of sodamide leads to the production of a dialkyl derivative identical with that obtained by Kipping's method from a substituted β-phenylpropionic acid; thus 2:2-*dimethyl*-1-*hydrindone*,

$$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CMe_2,$$

was prepared in 80% yield by warming an ethereal solution of hydrindone with sodamide in absence of air, boiling with methyl iodide for an hour, isolating the product, b. p. 116—120°/16 mm., and repeating the methylation, using benzene as the solvent. The compound was also obtained by the action of aluminium chloride on *β-phenyl-αα-dimethylpropionyl chloride*, m. p. 5°, b. p. 125—126°/15 mm. 2:2-Dimethylhydrindone forms magnificent crystals, m. p. 44—45°; when heated with sodamide in benzene it yields β-phenyl-αα-dimethylpropionamide. The *semicarbazone* forms needles, m. p. 209—210°.

2:2-*Diethylhydrindone*, $C_{13}H_{16}O$, has m. p. 7°, b. p. 138°/13 mm., and does not form a semicarbazone. The following compounds are described in connexion with its preparation.

β-Phenyl-α-ethylpropiophenone, $COPh\cdot CHEt\cdot CH_2Ph$, arising from the action of benzyl chloride on phenyl *n*-propyl ketone in presence of sodamide, has b. p. 183—185°/14 mm., and forms an *oxime*, m. p. 70°. *β-Phenyl-α-benzyl-α-propylpropiophenone*, $COPh\cdot CPr^{\alpha}(CH_2Ph)_2$, is also formed in this reaction, and crystallises in needles, m. p. 67—68°. *β-Phenyl-αα-diethylpropiophenone*, $COPh\cdot CEt_2\cdot CH_2Ph$, obtained as a liquid, b. p. 190—202°/13 mm., by ethylation of β-phenyl-α-ethylpropiophenone, slowly crystallises in tablets, m. p. 80—80·5°. *β-Phenyl-αα-diethylpropionyl chloride* has b. p. 148°/13 mm. W. O. W.

Synthesis of the Higher Indandiones. Martin Freund and Karl Fleischer (*Annalen*, 1910, **373**, 291—336).—Benzene and other aromatic hydrocarbons readily condense with diethylmalonyl chloride in the presence of aluminium chloride, yielding indandiones as the chief products in accordance with the equation:

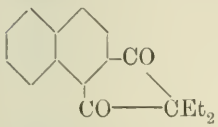
$$C_6H_6 + CEt_2(COCl)_2 = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CEt_2 + 2HCl,$$

carbon disulphide usually being employed as the solvent; thus equal molecular quantities of benzene and the chloride yield a very small amount of *γγ-dibenzoylpentane*, $CEt_2(COPh)_2$, m. p. 103—104°, the chief product being 2:2-*diethylindan*-1:3-*dione*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CEt_2$,

b. p. 147—156°/10 mm., D^{15} 1·062, which forms a *dioxime*, m. p. 142—144°, yields phthalic acid by oxidation with nitric acid at 130—140°, and benzoic acid by heating with concentrated potassium hydroxide. When two molecular proportions of benzene are employed in the condensation, a third product is obtained, *β-hydroxy-ββ-diphenyl-aa-diethylpropiolactone*, $CEt_2<^{CPh_2}_{CO-\!-}>O$, m. p. 89—90°.

Condensation with *p*-cymene yields only 4-*methyl*-2 : 2-*diethyl*-7-iso*propylindandione*, $C_6H_2MePr^{\beta}<^{CO}_{CO}>CEt_2$, m. p. 37—38·5°, the constitution of which follows from its oxidation to prehnitic acid by nitric acid at 130°.

With more complex hydrocarbons increasing difficulty is encountered in ascribing constitutions to the resulting indandiones. Naphthalene

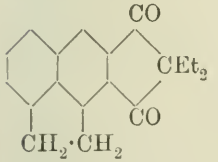


yields three isomeric products : I, a yellow *solid*, m. p. 79—81°, which receives the annexed constitution on account of its oxidation to prehnitic acid ; II, a colourless *solid*, m. p. 120·5—122°, in which condensation has occurred at positions 2 and 3 of the naphthalene nucleus, since boiling concentrated aqueous potassium hydroxide decomposes the substance, forming *β-naphthoyldiethylacetic acid*,

$$C_{10}H_7\cdot CO\cdot CEt_2\cdot CO_2H,$$

m. p. 128—130°, which is oxidised by nitric acid at 120—140° to trimellitic acid ; III, an *oil*, b. p. 210—212°/6 mm., which is very stable to alkali, and receives the only remaining possible constitution in which condensation has occurred in the *peri*-position.

The constitutions of the two indandiones obtained from acenaphthene



follow very much from analogy to those of the naphthindandiones; *a-diethylacenaphthindandione*, m. p. 153—155°, is yellow, and is converted by concentrated potassium hydroxide into *a-diethylacenaphthindandionic acid*, $C_{19}H_{20}O_3$, m. p. 163—164° ; it receives the annexed constitution. *β-Diethylacenaphthindandione*, m. p. 109—111°, is intensely yellow, and has the group $CEt_2<^{CO}_{CO}$ in positions 1 : 2.

The condensation of anthracene (without carbon disulphide) yields only *diethylanthraceneindandione*, $C_{21}H_{18}O_2$, m. p. 104—105°, which is oxidised by chromic and acetic acids to the *quinone*, $C_{21}H_{16}O_4$, m. p. 193—194°, and is converted by concentrated potassium hydroxide into *diethylanthraceneindandionic acid*, $C_{21}H_{20}O_3$, m. p. 209—210° (decomp.). The condensation of phenanthrene yields *diethylphenanthreneindandione*, $C_{21}H_{18}O_2$, m. p. 137—139°, b. p. 254—273°/10 mm., which is converted by potassium hydroxide into *diethylphenanthreneindandionic acid*, m. p. 155°, and by chromic and acetic acids into the *quinone*, $C_{21}H_{16}O_4$, m. p. 223—224°, which is further oxidised by the acids, when hot, to the *diethylindandione* of diphenic acid,

$$C_{12}H_6(CO_2H)_2<^{CO}_{CO}>CEt_2,$$

m. p. 235°. The condensation with retene yields *diethylreteneindandione*, $C_{25}H_{26}O_2$, m. p. 134—135°, which yields the *quinone*, $C_{25}H_{24}O_4$, m. p. 193—194°, by oxidation.

The condensation with thiophen yields two products, neither of which is an indandione: one is *γγ-dithiophenoylpentane*,

$$CEt_2(CO\cdot C_4SH_3)_2,$$

m. p. 152—153°; the other, *γ-thiophenoylpentane*,

$$CHEt_2\cdot CO\cdot C_4SH_3,$$

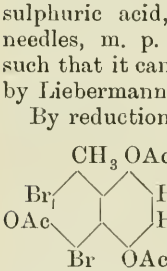
b. p. 146—147°/22 mm., D^{18} 1·058, and n_D 1·53153.

Many of these indandiones and indandionic acids develop characteristic colorations with concentrated sulphuric acid; tabulated lists of these are given. C. S.

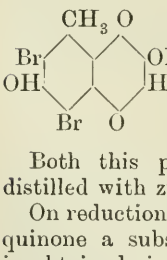
Constitution of β-Bromocarmin. Georg Rohde and G. Dorfmüller (*Ber.*, 1910, **43**, 1363—1370).—β-Bromocarmin was considered by von Miller and Rohde (Abstr., 1894, i, 94) to be a substituted bromohydroxy-α-naphthaquinone derivative; Liebermann and Voswinckel (Abstr., 1897, i, 539; 1909, i, 487) regarded it as an indone derivative.

β-Bromocarmin, when warmed with acetic anhydride and a drop of sulphuric acid, forms an *acetyl* derivative crystallising in yellow needles, m. p. 229°; this is no longer acid, and the composition is such that it cannot be derived from a substance of the formula proposed by Liebermann and Voswinckel.

By reduction of β-bromocarmin with zinc dust and acetic acid and subsequent acetylation, a *compound*, $C_{17}H_{14}O_6Br_2$, crystallising in minute, colourless needles, m. p. 208°, is obtained, which has the annexed formula, agreeing with the constitution of Miller and Rhode, but which is not in agreement with the indone structure.



Hydrolysis and oxidation by means of alkaline hydrogen peroxide yields a *substance*, crystallising in orange prisms, m. p. 258°, in which probably a hydroxyl group has entered the quinone nucleus (annexed formula).



On acetylation, greenish-yellow needles, m. p. 233°, of a *diacetyl* derivative were obtained. The hydrolysis and oxidation product is only slightly attacked by bromine, small quantities of α-bromocarmin being formed.

Both this product and β-bromocarmin yield naphthalene when distilled with zinc dust.

On reduction and subsequent acetylation of bromohydroxy-α-naphthaquinone a substance crystallising in colourless needles, m. p. 159°, is obtained, in which neither hydroxyl nor bromine is replaced by hydrogen. This behaviour is attributed to the negative groups in the second nucleus of bromohydroxynaphthaquinone. E. F. A.

Action of Magnesium Derivatives of *o*- and *p*-Bromoanisole on Anthraquinone and β-Methylanthraquinone. Albin Haller and A. Comtesse (*Compt. rend.*, 1910, **150**, 1290—1295. Compare Abstr., 1904, i, 314, 659, 660; Guyot and Staehling, Abstr., 1905, i, 885; 1906, i, 17).—The organo-magnesium derivatives of *o*- and

p-bromoanisole react with anthraquinone and methylanthraquinone in the same manner as the magnesium derivatives of benzene and naphthalene already studied.

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*anisyldihydroanthracene*,

$$C_6H_4<\begin{matrix}C(C_6H_4\cdot OMe)(OH)\\C(C_6H_4\cdot OMe)(OH)\end{matrix}>C_6H_4,$$

obtained from anthraquinone and magnesium *p*-anisole bromide, is a colourless, microcrystalline substance, m. p. 267°. Sulphuric acid develops a red coloration, changing to violet, then to blue, and becoming green on dilution. Dimethylaniline gives a blue coloration, changing to rose-violet. The *diethyl ether* has m. p. 280—281°.

9 : 10-*Dihydroxy*-9 : 10-*di*-o-*anisyldihydroanthraquinone*, occurring in microscopic crystals, m. p. 285°, forms a blue solution in sulphuric acid, changing to green, and becoming brown on heating or dilution. When boiled with zinc and glacial acetic acid it yields *di*-o-*anisylanthracene*, $C_6H_4<\begin{matrix}C(C_6H_4\cdot OMe)\\|\\C(C_6H_4\cdot OMe)\end{matrix}>C_6H_4$, crystallising in yellow needles, m. p. 280—281°. *Di*-p-*anisylanthracene* forms yellow needles, m. p. 279—280°, and, like the ortho-compound, dissolves sparingly in organic solvents, giving bluish-violet solutions, which show magnificent fluorescence.

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*anisyl*-2-*methyldihydroanthracene*,

$$C_6H_4<\begin{matrix}C(C_6H_4\cdot OMe)(OH)\\C(C_6H_4\cdot OMe)(OH)\end{matrix}>C_6H_3Me,$$

prepared from β-methylanthraquinone, separates from benzene in efflorescent crystals, m. p. 208°; with sulphuric acid it develops an intense, eosin-red coloration, changing to blue, and on dilution to green. Dimethylaniline gives a green coloration, changing to brown. The isomeric *di*-o-*anisyl* compound forms efflorescent crystals, m. p. 260°, and gives an intense malachite-green coloration with sulphuric acid; glacial acetic acid and dimethylaniline give a brilliant-green coloration, changing to olive. *Di*-p-*anisyl*-β-*methylanthracene* crystallises in yellow needles, m. p. 214—215°; its solutions are reddish-violet and highly fluorescent. *Di*-o-*anisyl*-β-*methylanthracene* resembles the para-isomeride, and has m. p. 165—167°.

Attempts to convert the foregoing diols into diphenols by heating with hydrogen bromide were unsuccessful. W. O. W.

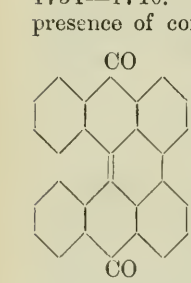
Attempts to Prepare Thiazine Dyes of the Anthraquinone Series. Eduard Laubé and J. Libkind (*Ber.*, 1910, 43, 1730—1734). —Whereas diamino-1-anilinoanthraquinone reacts readily with sulphur, forming a thiazine dye, the 2-anilino-derivative gives a variety of products, and only very little sulphur compound. Apparently, an amino-group is eliminated, and the basic properties are much lessened, so that it is doubtful whether the sulphur compounds are true thiazine dyes.

1-*op*-Dinitroanilinoanthraquinone, prepared from aminoanthraquinone and chlorodinitrobenzene in presence of copper acetate or copper powder, separates in well formed, brown, lustrous needles, m. p. 341° (corr.). The corresponding 2-op-*dinitroanilinoanthraquinone* crystallises in beautiful yellow, lustrous needles, m. p. 275° (corr.).

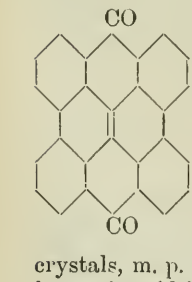
1-op-*Diaminoanilinoanthraquinone*, obtained by reducing the nitro-compound with sodium sulphide, forms small, reddish-violet crystals, m. p. above 350°, which give a reddish-violet, metallic streak on glazed porcelain. 2-op-*Diaminoanilinoanthraquinone* forms black needles, m. p. 255°, and makes a brownish-red streak on porcelain.

The 1-*anthrathiazine*, $C_6H_4\langle^{CO}_{CO}\rangle C_6H_2\langle^{NH}_{S}\rangle C_6H_3\cdot NH_2$, is obtained from 1-*op*-diaminoanilinoanthraquinone by heating it at 150—200° with sulphur and sodium sulphide. It dyes cotton in fast green shades. The corresponding dye from the 2-anilino-compound is obtained in small quantities only, and dyes cotton in fast brown shades. E. F. A.

Vat Dyes of the Anthracene Series. XV. *meso*Benzdianthrone (Helianthrone), *meso*Naphthadianthrone, and a New Method of Preparing Flavanthren. Roland Scholl, Johannes Mansfeld [and, in part, Julius Potschiwauschieg] (*Ber.*, 1910, **43**, 1734—1746. Compare this vol., i, 264, 272).—Copper powder in presence of concentrated sulphuric acid at the ordinary temperature acts as a reducing agent on dianthraquinonyl, eliminating two oxygen atoms and forming a binuclear quinone, which it is proposed to name 1 : 9-, 1′ : 9′-, or *meso*benzdianthrone (annexed formula). The compound was at first described under the name helianthrone. It contains the two chromophores in conjugated position, and, accordingly, should give only one reduction product of the anthrahydroquinone type, namely, a dihydro-compound. Only one, a green, reduction vat is formed by *meso*benzanthrone.



When heated with anhydrous aluminium chloride for a short time at 140—145°, it is quantitatively converted into 1 : 9 : 8-, 1′ : 9′ : 8′-, or *meso*naphthadianthrone (annexed formula). On nitrating 1 : 1′-dianthraquinonyl, a mixture of dinitro-derivatives is obtained, which, when reduced with potassium sulphide, shows the presence of small quantities of flavanthren. The unknown 2 : 2′-*dinitro*-1 : 1′-*dianthraquinonyl* must have been formed and reduced to the corresponding 2 : 2′-*diamino*-derivative, which undergoes spontaneous change into flavanthren.



1 : 1′-Dianthraquinonyl was prepared by reduction of iodoanthraquinone in yellow or brownish-yellow crystals, m. p. 340—345°. The *tetrabromide*, produced by bromination in acetic acid in presence of iodine, forms dark needles. On nitration, in addition to the 2 : 2′-dinitro-derivative which was not isolated, two other isomerides in about equal quantities were obtained. *α-Dinitro*-1 : 1′-*dianthraquinonyl* is a yellow powder, m. p. above 360°, and insoluble in boiling acetic acid. On reduction, the corresponding *diamino*-compound, a glistening, red powder, is formed. *β-Dinitro*-1 : 1′-*dianthraquinonyl* is a yellow powder, decomp. 240°, soluble in boiling acetic acid. The *diamino*-compound is a dark brownish-red powder.

1 : 1′-Dianthraquinonyl may be reduced to meso*benzdianthrone* by

means of zinc dust and acetic acid at 60—70°, stannous chloride at 150°, zinc dust and fused zinc chloride at 280—290°, alcoholic potassium hydroxide at 200°, or, best of all, copper powder and concentrated sulphuric acid. *meso*Benzdianthrone dissolves in organic solvents to yellow solutions with a green fluorescence. *Tetrabromo*meso*dianthrone* forms yellowish-brown needles, and yields a green reduction vat which dyes glistening, golden-yellow shades.

The green vat produced by reducing *meso*benzdianthrone with hot alkaline sodium hyposulphite is a dihydro-derivative, since it forms *di*-p-*bromobenzoyldihydro*meso*benzdianthrone* on treatment with bromobenzoyl chloride.

meso*Naphthadianthrone* forms brown needles from nitrobenzene; it dissolves in concentrated sulphuric acid with a red coloration and brown fluorescence. E. F. A.

Reduction Products of *meso*Benzdianthrone (Helianthrone). Julius Potschiwauscheg (*Ber.*, 1910, 43, 1746—1748).—*meso*Benzdianthrone when shaken with acetic anhydride and zinc dust at the ordinary temperature yields *diacetyldihydro*meso*benzdianthrone* in the form of a brown powder soluble in chloroform or acetic anhydride with an olive-green or green fluorescence, and in concentrated sulphuric acid with a green coloration which becomes violet above 200°.

Reduction of *meso*benzdianthrone in boiling acetic anhydride yields *tetrahydro*meso*benzdianthrone* in the form of a black, amorphous *acetyl* derivative, which is hydrolysed by methyl-alcoholic potassium hydroxide. The blackish-brown, amorphous powder shows a brownish-green fluorescence in chloroform; the solution in concentrated sulphuric acid is green, and becomes brown on heating at 240—260°.

When the reduction is prolonged for thirty hours, the *acetyl* derivative of *hexahydro*meso*benzdianthrone* is obtained as a brown, amorphous powder, and hydrolysed by prolonged boiling with methyl-alcoholic potassium hydroxide. E. F. A.

Dihydrocuminyl Alcohol, Nerol, and Terpineol in Bergamot Oil. Fritz Elze (*Chem. Zeit.*, 1910, 34, 538).—In preparing "terpeneless bergamot oil," an ester fraction, D^{15} 0·896, $\alpha = -10°45'$, was obtained, which on hydrolysis yielded a mixture of alcohols, D^{15} 0·890, $\alpha = -10°$. From this, dihydrocuminyl alcohol and nerol were isolated by conversion into phthalic acid esters, hydrolysis of these, and fractionation of the resulting mixture under reduced pressure. The portion of the original alcoholic mixture which did not react with phthalic anhydride was identified as terpineol by conversion into the phenylurethane. T. A. H.

Constituents of Ethereal Oils. Eksantalic Acid, $C_{12}H_{18}O_2$, Eksantalal, $C_{12}H_{18}O$, and Derivatives. Friedrich W. Semmler (*Ber.*, 1910, 43, 1722—1725. Compare Abstr., 1909, i, 239).—To establish the constitution of eksantalic acid the crude product obtained by the oxidation of santalol with permanganate was reduced with sodium and alcohol to *dihydroeksantalic acid*, $C_{12}H_{20}O_2$, b. p. 164—166°/10 mm. The methyl ester was further reduced to *dihydroeksantalol*, $C_{12}H_{22}O$, b. p. 140—142°, D^{20} 0·9689, n_D 1·48905.

The crude ozonide of santalol was decomposed by steam, and two products obtained, one being *eksantaloide*, m. p. 157°, and the other, separated by means of the bisulphite compound, *eksantalal*, $C_{12}H_{18}O$, b. p. 109—110°/10 mm., D^{20} 0·9845, n_D 1·48519, $\alpha_D = +13·5°$ (in 100 mm. tube). Heating with acetic anhydride and sodium acetate forms enol-*eksantalal acetate*, $C_{12}H_{17}O{\cdot}CO{\cdot}CH_3$, b. p. 130—132°/10 mm., D^{20} 1·018, which on oxidation with permanganate gives *noreksantalic acid*,

$$C_{11}H_{16}O_2,$$

b. p. 143—145°/10 mm., m. p. 93°, α_D −12·3° (100 mm. tube, 50% solution). The *methyl* ester has b. p. 102—104°/10 mm., D^{20} 1·023, n_D 1·47348, α_D −25·5° (100 mm. tube). E. F. A.

Chemical Action of Light. XVII. Giacomo L. Ciamician and Paul Silber (*Ber.*, 1910, 43, 1340—1350; *Atti R. Accad. Lincei*, 1910, [v], 19, i, 532—539).—Camphor in dilute aqueous alcoholic solution in sealed tubes was exposed to the action of light for some months. The products of the reaction were acetaldehyde and campholenaldehyde, $C_{10}H_{16}O$, which forms a hydroxamic acid, $C_{10}H_{17}O_2N$, crystallising in large, colourless, fatty, lustrous plates, m. p. 118°, and is hydrolysed by dilute sulphuric acid to campholenic acid and dihydrocampholenolactone. The third product of the action of light is a *ketone*, $C_{10}H_{16}O$, which is an oil, b. p. 203—204°, and forms a *semicarbazone*, crystallising in colourless, minute needles, m. p. 151—152°. On oxidation, the ketone forms a *dibasic acid*, $C_{10}H_{16}O_5$, crystallising in colourless prisms, m. p. 133—134°.

Fenchone under similar conditions gave rise to carbon monoxide in considerable quantity, and to small quantities of *fenchone hydrate*, $C_{10}H_{18}O_2$, crystallising in plates, m. p. 138—139°. This glycol forms a *dibenzoate*, m. p. 99°, and a *dicarbanilate*, m. p. 206° (decomp.).

Exposure to light has practically no effect on methyl *iso*butyl ketone, mesityl oxide, or methylheptenone, but pinacolin undergoes decomposition into butylene and acetaldehyde. E. F. A.

Caryophyllene. II. Carl W. Haarmann (*Ber.*, 1910, 43, 1505—1510. Compare Abstr., 1909, i, 400).—Caryophyllene glycol, m. p. 120°, which had been kept in a closed bottle for four years, was found to be largely transformed into a syrup, probably $C_{14}H_{22}O_3$, and a mixture of two monobasic acids, $C_{14}H_{22}O_5$. The one acid is identical with that already described (*loc. cit.*) as melting at 201—202°; the other is much more readily soluble in ether, crystallises from acetone, and has m. p. 152°. Both acids, when heated with 5% sulphuric acid, lose water and yield anhydro-acids, $C_{14}H_{20}O_4$, melting respectively at 102—103° and 106°, whereas a mixture of the two has m. p. 74—78°.

A dibasic *acid*, $C_{14}H_{20}O_5$, is formed when the acid 201—202° is oxidised with nitric acid (D = 1·48); it forms glistening, hard crystals, m. p. 225°. When the acid, m. p. 152°, is oxidised in a similar manner, a dibasic *acid*, $C_{14}H_{20}O_5$, is obtained as slender needles, m. p. 182°. This acid is quite stable towards permanganate and mixtures of nitric and sulphuric acids.

The acids m. p. 201—202° and 152° can be obtained in the

proportions 1 : 8 by shaking an ethereal solution of carophyllene glycol with a few drops of concentrated sulphuric acid and oxidising the resulting oil with 5% permanganate solution.

When the glycol is oxidised with permanganate, the only acid product formed is the one with m. p. 171°. The statement that two acids, m. p. 201—202° and 162°, are formed is incorrect, as their formation in previous experiments was due to the fact that the glycol had been kept for some time and had undergone change.

J. J. S.

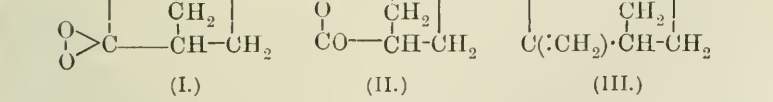
Rotatory Power of Pinene Hydrochloride. Gustave Vavon (*Compt. rend.*, 1910, **150**, 1428—1430. Compare this vol., i, 400; Ahlström and Aschan, Abstr., 1906, i, 442).—A comparison has been made in the case of a number of fractions obtained by crystallisation of the hydrochlorides from French, German, and American turpentines between the rotatory power of the hydrochloride and that of the corresponding pinene and of the product of hydrogenation. The results are given in tabular form, and show that α- and β-pinene yield equal amounts of the same hydrochloride. Similar results have been obtained from a study of the hydrobromides.

W. O. W.

Oxidation of Camphene with Ozone. Carl D. Harries and John Palmén (*Ber.*, 1910, **43**, 1432—1434. Compare Semmler, Abstr., 1909, i, 170).—When an acetic acid solution of pure camphene is treated with ozone at 10°, and the solution of the ozonide then heated on the water-bath, both dimethylnorcampholide—50% (Komppa and Hintikka, Abstr., 1909, i, 301)—and camphenilone are obtained.

The dimethylnorcampholide (δ-hydroxycamphenilonolactone) and not the free hydroxy-acid is regarded as the direct product of decomposition, and its formation is attributed to the peroxide decomposition of the ozonide into peroxide (I), which is transformed readily into the isomeric lactone (II) (compare Harries and Franck, Abstr., 1909, i, 132).

The formation of this lactone is in harmony with Tiemann's camphene formula (III), and the conversion of bornyl chloride into camphene involves a pinacoline transformation.



(I.) (II.) (III.)

Camphenilone was isolated as its *semicarbazone*, $C_{10}H_{17}ON_3$, m. p. 222—223°.

J. J. S.

Loango Copal. M. Willner (*Arch. Pharm.*, 1910, **248**, 265—276).—Loango copal, acid number 106·4—114·8 (direct), 114·8—120·4 (indirect), and saponification number 126·0—134·4 (hot), 142·8—154·0 (cold, after twenty-four hours), dissolves completely in

pyridine or quinoline. In its examination it is extracted first by ether, which dissolves 74·9%, and then with ether-alcohol, which dissolves the remainder with the exception of about 2%, consisting of inorganic matter containing sodium, potassium, calcium, magnesium, iron, and silica.

The ethereal abstract is treated successively with 0·5% ammonium carbonate, sodium carbonate, and sodium hydroxide. From the ammonium carbonate solution about 30% of crude acids have been obtained, from which the following have been isolated. *α-Loangocopalic acid*, $C_{20}H_{36}O_2$, m. p. 134°, a monobasic acid containing one ethylenic linking, forms a lead salt insoluble in alcohol, and has acid number 154·0—158·2 (direct), 164·9—165·8 (indirect), saponification number 177·2—177·8 (cold), 180·0—181·4 (hot), and iodine number 78·4—80·4. *β-Loangocopalic acid*, $C_{15}H_{30}O_2$, m. p. about 56°, a monobasic acid containing one ethylenic linking, forms a lead salt soluble in alcohol, and has acid number 192·1—194·3 (direct), 198·2—199·9 (indirect), saponification number 203·5—204·7 (hot), 199·4—201·3 (cold), and iodine number 105·3—109·4.

Loangocopalolic acid, $C_{18}H_{34}O_2$, m. p. 60°, obtained from the crude acids isolated from the sodium carbonate extract, has acid number 185·1—187·3 (direct), 191·2—193·4 (indirect), saponification number 192·3—196·0 (hot), 199·1—200·2 (cold), and iodine number 88·7—88·1, and forms a lead salt which is insoluble in alcohol.

From the ether-alcohol solution, 0·5% sodium hydroxide extracts *β-loangocopal resin*, $C_{23}H_{46}O_2$, m. p. 200°, which is insoluble in hot alcohol, and *loangocopalinic acid*, $C_{24}H_{44}O_2$, m. p. 165°, which is soluble in hot alcohol, and has acid number 146·2—148·7 (direct), 153·2—154·3 (indirect), saponification number 161·5—163·2 (cold), 166·7—168·9 (hot), and iodine number 70·2—71·6. C. S.

Sierra Leone Copal. M. Willner (*Arch. Pharm.*, 1910, 248, 285—293).—Sierra Leone copal, acid number 108·6—114·4 (direct), 121·2—126·6 (indirect), saponification number 145·9—150·1 (hot), 142·8—146·7 (cold), dissolves completely in quinoline. In its examination it is extracted first by ether, which dissolves 63·4%, then by ether-alcohol, which dissolves the remainder with the exception of about 7%, the inorganic constituents of which contain sodium, potassium, calcium, magnesium, and silica.

The ethereal extract is treated successively with 0·5% ammonium carbonate, sodium carbonate, and 1% potassium hydroxide. From the crude acids isolated from the ammonium carbonate solution, *leonecopalic acid*, $C_{25}H_{48}O_3$, m. p. about 142°, has been obtained as an amorphous powder; it has acid number 136·4—138·0 (direct), 142·3—144·2 (indirect), saponification number 150·6—151·5 (hot), 154·0—155·7 (cold), and iodine number 64·8—65·2, and forms a lead salt which is insoluble in alcohol. *Leonecopalolic acid*, $C_{21}H_{38}O_2$, m. p. about 133°, obtained from the crude acids isolated from the sodium carbonate extract, has acid number 157·9—159·6 (direct), 164·4—165·2 (indirect), saponification number 171·4—173·0 (hot), 176·7—178·6 (cold), and

iodine number 76·7—79·6, and forms a lead salt which is insoluble in alcohol.

From the ether-alcohol solution, 0·1% sodium hydroxide extracts *leonecopalinic acid*, $C_{14}H_{24}O_2$, m. p. about 184°, which has acid number 187·9—190·1 (direct), 194·0—195·5 (indirect), saponification number 205·5—207·5 (hot), 202·2—206·6 (cold), iodine number 110·0—111·7, and forms a lead salt soluble in alcohol, and *β-leonecopal resin*, $C_{14}H_{26}O_2$, m. p. about 195°, a white, amorphous powder insoluble in ether. C. S.

Glucoside of Ecballium elaterium. Armand Berg (*Bull. Soc. chim.*, 1910, [iv], **7**, 385—388).—The author has stated previously (Abstr., 1898, ii, 447) that elaterin exists in fruit of the squirting cucumber for the most part, if not entirely, in the form of an amorphous, yellow glucoside, $C_{34}H_{48}O_{12}$, which is decomposed by a specific enzyme, elaterase, also occurring in the fruit, yielding elaterin and dextrose. Power and Moore (Trans., 1909, **95**, 1985) were unable to confirm the existence of this glucoside. The author has therefore repeated his experiments, and has confirmed his previous results. When boiled with dilute sulphuric acid the glucoside is hydrolysed, yielding acetic acid, dextrose, and a resinous product, probably consisting of anhydroelateridin with some impurity (compare Hemmelmayr, Abstr., 1906, i, 973). T. A. H.

Action of Silver Oxide on Elaterin. Armand Berg (*Compt. rend.*, 1910, **150**, 981—983).—Dry silver oxide is without action on elaterin; in presence of water, however, it brings about simultaneous oxidation and hydrolysis. The chief product is an amorphous, yellow substance, *elateridoquinone*, $C_{26}H_{36}O_7$, which is insoluble in alkalis, and does not develop a coloration with ferric chloride. The yellow colour is discharged by hydrochloric acid. Acetic acid, together with small quantities of a phenolic compound and an acid of unknown composition, have also been recognised amongst the products of the reaction. With elateridin, silver oxide yields traces of a substance insoluble in alkalis.

These observations throw doubt on the view that elaterin is an aldehydic compound. W. O. W.

Chlorophyll. IX. Oxidation of Chlorophyll Derivatives. Richard Willstätter and Yasuhiko Asahina (*Annalen*, 1910, **373**, 227—238. Compare this vol., i, 126).—Phylloporphyrin, pyrroporphyrin, rhodoporphyrin, and phytochlorin, when oxidised with lead dioxide and sulphuric acid, chromic acid, or Caro's acid, yield hæmatic acid and methylethylmaleinimide (compare Küster, Abstr., 1901, i, 58, 298; 1906, i, 337), together with smaller decomposition products, such as acetic acid and carbon dioxide. The quantities of hæmatic acid and methylethylmaleinimide formed have been carefully estimated, with the result that one mol. of a porphyrin derived from chlorophyll is found to yield 1 mol. of hæmatic acid and 2 mols. of methylethylmalein-

imide. Since hæmin when oxidised probably yields only 2 mols. of hæmatic acid (compare Küster, *loc. cit.*; Piloty, Abstr., 1909, i, 539), and does not yield methylethylmaleinimide, it follows that at least two of the four pyrrole nuclei in hæmin are different from those in the porphyrins derived from chlorophyll. W. H. G.

Determination of the Constitution of the Coumaran Ketones. Charles Marschalk (*Ber.*, 1910, 43, 1695—1700. Compare Abstr., 1907, i, 950).—A direct proof of the constitution of the coumaran ketones was sought in the opening of the oxygen ring, but this does not readily take place. Coumaran, after heating with hydriodic acid, has the ring opened, forming *o*-ethylphenol, but 2-phenylcoumaran behaves altogether differently. It is now shown that benzylcoumaran, after heating with hydrogen iodide and subsequent treatment with alcoholic hydrogen chloride and zinc dust, forms *benzyl-o-ethylphenol*, $CH_2Ph\cdot C_6H_3Et\cdot OH$, a colourless oil, b. p. 323°/718 mm. By the action of methyl sulphate this is converted into p-*benzyl-o-ethylanisole*, $CH_2Ph\cdot C_6H_3Et\cdot OMe$, a colourless oil, b. p. 308—312°/720 mm., $n = 1{\cdot}566$. This constitution was established by the synthesis of the compound from *o*-ethylanisole, which was converted into the *p*-benzoyl derivative, and this reduced with sodium and alcohol to *p*-benzyl-*o*-ethylanisole. It is, therefore, established that on coupling aromatic acid chlorides with coumaran, the acid residue enters in the para-position (4) to the bridge carbon atom. E. F. A.

Preparation of Thionaphthen Derivatives. Badische Anilin- & Soda-Fabrik (D.R.P. 221465).—When compounds having the general formula $R<^{S\cdot CH=CH\cdot S}_{CO_2R_1\ \ R_1O_2C}>R$, where R is a substituted benzene or naphthalene residue, R_1 a metal, alkyl or aryl group, are heated in the presence of alkalis or alkyloxides, either with or without the addition of such reducing agents as zinc, iron or sodium hyposulphite, they yield substantive dyes of the thionaphthen series.

3-Oxy-(1)-thiosalicylic acid is prepared by heating an intimate mixture of acetylene bis-*o*-thiolbenzoic acid and sodium hydroxide during half an hour at 220—230°, whilst the corresponding naphthalene derivative is similarly prepared from acetylene-bis-1-thiol-2-naphthoic acid.

F. M. G. M.

Agmatine. Albrecht Kossel (*Zeitsch. physiol. Chem.*, 1910, 66, 257—251).—Agmatine, $C_5H_{14}N_4$, is a base which can be obtained from herring spawn after treatment with sulphuric acid at 4 atmospheres pressure in the autoclave. It was finally obtained as a crystalline aurichloride, or sulphate, and analysed. It is formed from arginine, and differs from it by CO_2. This is shown in the following formulæ:

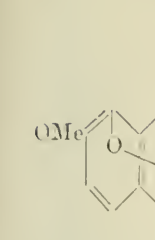
$NH_2\cdot C(NH)\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$ arginine.

$NH_2\cdot C(NH)\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$ agmatine.

W. D. H.

Berberine. I. Berberrubine. Gustav Frerichs (*Arch. Pharm.*, 1910, 248, 276—284).—*Berberrubine*, $C_{19}H_{15}O_4N$, m. p. about 285°, is obtained by heating a mixture of berberine hydrochloride and carb-

amide for half an hour at 200°, pouring the partially cooled mass into water, and extracting with chloroform; the crude base obtained by the evaporation of the chloroform is purified through the hydrochloride. The pure base separates from water in dark red leaflets and flat needles containing $3H_2O$; the anhydrous substance is almost black, and has an extraordinary power of absorbing water. Berberine hydriodide is obtained by the addition of methyl iodide to berberrubine, which behaves like an internal phenoxide of the annexed constitution, assuming that the elimination of methyl alcohol from berberine occurs at the nearest methoxyl group.



The basic character of berberrubine is not great; it forms yellow, crystalline salts with strong acids, of which the *hydrochloride* and the *sulphate* are described; these are easily decomposed by alkali hydroxides or carbonates, or by ammonium hydroxide. The base is reduced to colourless *tetrahydroberberrubine*, $C_{19}H_{19}O_4N$, m. p. 167—168°, by zinc in the presence of sulphuric and acetic acids.

C. S.

The Alkaloid of Pseudocinchona africana. Hydrolysis by Alkalis. Ernest Fourneau (*Compt. rend.*, 1910, **150**, 976—978. Compare Abstr., 1909, i, 600).—The new alkaloid recently obtained from the bark of *Pseudocinchona africana* closely resembles yohimbine except in its optical rotatory power. Sodium ethoxide in alcoholic solution converts it into an *acid*, $C_{20}H_{24}O_3N_2$, isomeric with the compound obtained in the same way from yohimbine (Spiegel, Abstr., 1903, i, 274). This substance crystallises from alcohol in slender, brilliant needles, m. p. below 300°, and is obtained in a hydrated form when precipitated by acids from its solutions in alkalis. The *silver* salt, $C_{20}H_{23}O_7N_2Ag,H_2O$, is a yellow powder. W. O. W.

Corycavine. G. Otto Gaebel (*Arch. Pharm.*, 1910, **248**, 207—250).—In addition to the twelve alkaloids which have already been isolated from the rhizomes of *Corydalis cava*, the author has obtained a small amount of yet another *alkaloid*, $C_{25}H_{25}O_7N$ (?), m. p. 193—194°, $[\alpha]_D$ 100° in chloroform, the *hydrobromide* of which decomposes at 224°.

It is noteworthy that protopine has never been isolated from *Corydalis cava*, although it is present in almost all other species of the Papaveraceæ, and is regarded by Schmidt as the parent of the other Papaveraceæ alkaloids.

Having at his disposal a large quantity of crude material, the author has worked up 50 grams of crude corycavine, which is finally purified by crystallisation from hot alcohol-chloroform; the mother liquor contains the new alkaloid, m. p. 193—194°.

Most of the physical and the chemical properties of corycavine recorded by previous investigators are confirmed by the author; the m. p. is given as 218—219°, and the *aurichloride*, $C_{23}H_{23}O_6N,HAuCl_4$, has m. p. 178—179° (decomp.). The absence of hydroxyl and of

methoxy-groups is confirmed. The presence of at least one methylenedioxy-group is proved by Weber and Tollens' process. The nitrogen is monomethylated, and is present as tervalent nitrogen in a monocyclic system, as is proved, not only quantitatively by Herzig and Meyer's method of estimating methylimino-groups, but also by the behaviour of corycavine methiodide, which, submitted to Hofmann's process of exhaustive methylation, yields successively corycavinemethine, corycavinemethine methiodide, and a non-nitrogenous, amorphous substance and trimethylamine. *Corycavinemethine*, $C_{24}H_{25}O_6N$, m. p. 153—154°, is obtained by heating corycavine methiodide with a large excess of concentrated sodium hydroxide. It separates from alcohol in white needles, develops with concentrated hydrochloric acid an intense brown, then green, and finally deep blue coloration, decolorises bromine, and yields by heating with methyl iodide, *corycavinemethine methiodide*, $C_{25}H_{28}O_6NI$, m. p. 218—219° (decomp.), which is converted by distillation with concentrated sodium hydroxide into trimethylamine and an amorphous *substance*, which does not contain nitrogen and is practically insoluble in the usual organic solvents.

Corycavine, suspended in 100 times the quantity of water, and submitted for five to six days to reduction by hydrochloric acid and zinc dust at the temperature of boiling water, yields a mixture of two bases which partly remain in the liquid and partly separate as zincichlorides. One of the bases, which is soluble in ether, is a tertiary *base*, $C_{22}H_{25}O_4N$ (?), m. p. 125°, which forms well crystallised salts, contains a methylenedioxy-group, has a molecular weight of 368 by the ebullioscopic method in chloroform and also by the analysis of the *aurichloride*, and is probably formed at the expense of a methylenedioxy-group in corycavine, which therefore contains at least two such groups. The other base, the salts of which are not decomposed by ammonium hydroxide, is isolated by treating the hot aqueous solution of the zincichlorides (or the original mother liquor) with ammonium hydroxide, extracting the soluble base with ether, filtering the aqueous solution, acidifying it with acetic acid, and treating it with concentrated potassium iodide, whereby the *hydriodide* is precipitated. The *bromide*, *nitrate*, and *aurichloride*, m. p. about 185° (decomp.), are described. The pure base has not been analysed, but the intensely bitter taste of its salts, their stability to alkalis, and the formation of a new tertiary base by boiling the chloride with sodium hydroxide, indicate that the base is a quaternary ammonium hydroxide or a betaine thereof.

The oxidation of corycavinemethine in acetone at 0° by potassium permanganate yields, in addition to a small quantity of a *base*, m. p. 195—196°, an *acid*, $C_{18}H_{15}O_7N$, m. p. 110—111° (decomp.), which is apparently monocarboxylic. C. S.

Papaverine and Cryptopine. Amé Pictet and G. H. Kramers (*Ber.*, 1910, 43, 1329—1335).—Commercial papaverine shows a characteristic deep bluish-violet coloration with cold concentrated sulphuric acid, and gives more or less characteristic colorations with other alkaloid reagents. Synthetical papaverine, however, gives none of

these colorations. Commercial papaverine can be readily purified by means of the acid oxalate, $C_{20}H_{21}O_4N,H_2C_2O_4$, which crystallises in stellar aggregates of needles, m. p. 196°. The papaverine obtained from this by means of sodium hydroxide no longer gives the colour reactions which are due to admixture to the extent of 4% with another alkaloid, cryptopine (compare T. and H. Smith, *Pharm. J.*, 1867, [ii], 8, 595, 716; Hesse, this Journ., 1871, 1065).

Cryptopine crystallises in hexagonal prisms or plates, m. p. 218°. The dichromate forms minute, yellow prisms; the *picrate* forms long needles, grouped like a paint-brush, m. p. 215°; the *mercurichloride* is colourless, m. p. 185°; the *aurichloride* crystallises in brownish-yellow needles, which blacken at 200°, m. p. 205°; the *platinichloride* forms yellow, concentrically-grouped needles, m. p. 204° (decomp.).

Cryptopine is a saturated base, and is not attacked by hydrogen; the stannichloride crystallises in needles, m. p. 190° (decomp.). It contains two methoxyl groups and one methyl attached to nitrogen. It probably contains the methylenedioxy-group, $CH_2<^{O-}_{O-}$, as it gives a green coloration and the characteristic absorption spectrum with sulphuric and gallic acids. It contains neither phenol nor alcoholic hydroxyl, nor a keto-group. E. F. A.

Compound of Acetylbromoglucose and Pyridine. Emil Fischer and Karl Raske (*Ber.*, 1910, 43, 1750—1753).—Analogous to chlorodimethyl ether, β-acetylbromoglucose combines with pyridine to form *tetra-acetylglucosepyridinium bromide*. This crystallises in colourless, obliquely-cut prisms, m. p. 174° (corr.), $[\alpha]_D^{20}$ −6·43° (±0·2°). The crystallisation is greatly facilitated by the addition of a little phenol to the reaction mixture. The aqueous solution is neutral towards litmus, and reduces Fehling's solution only very feebly. When shaken with silver oxide, the free *base* is obtained, and remains as a syrup on evaporation. The only sparingly soluble salt is the *hydrogen ferrocyanide*, crystallising in stellar aggregates or bunches of needles, which are at first faintly yellowish-green, but become blue after a time or on crystallisation from hot water.

In addition to the crystalline tetra-acetylglucosepyridinium bromide, an amorphous, probably stereoisomeric, product of different rotation is obtained. E. F. A.

Salts of a Hexa-acetatotripyridinetrichromi-Base. Rudolf F. Weinland and Ernst Gussmann (*Zeitsch. anorg. Chem.*, 1910, 67, 167—182).—When pyridine is added to a concentrated solution of hexa-acetatotrichromic diacetate (Weinland and Dinkelacker, Abstr., 1909, i, 757) and the solution is warmed, the diacetate of a new base containing 3 mols. of pyridine is obtained. The mother liquor contains a basic acetate, $Cr_3(OAc)_3(OH)_3,9H_2O$, which will be described in a further communication.

The diacetate is obtained free from the accompanying pyridine acetate by precipitating with sodium acetate, and serves for the preparation of the other salts. All of these contain six acetic residues, whatever be the conditions of preparation, and these residues are therefore considered to form part of the cation complex.

The salts with colourless acids are pale green, but concentrated solutions are dark red, becoming pale green on dilution. Some of the salts are very sparingly soluble. The secondary and tertiary salts have an acid reaction, but the primary salts are neutral. The base may be prepared by the action of silver oxide on the iodide, and forms an unstable, alkaline solution.

Hexa-acetatotripyridinetrichromic triacetate,

$$\left[\begin{matrix}(OAc)_6\\ Cr_3\ 3Py\\ (OH_2)_2\end{matrix}\right]OAc_3,7H_2O,$$

prepared by precipitating the crude acetate with sodium acetate and acetic acid, forms small, green needles, readily soluble in water. The mono- and di-acetates were not completely separated. The *iodide*, $\left[\begin{matrix}(OAc)_6\\ Cr_3\ 3Py\\ (OH)_2\end{matrix}\right]I$, prepared by precipitation of the acetate solution with potassium iodide, forms almost insoluble, very pale green crystals. The *chloride-acetate*, $\left[\begin{matrix}(OAc)_6\\ 3Py\\ Cr_3\ OH_2\\ OH\end{matrix}\right]\begin{matrix}Cl\\ OAc\end{matrix},6H_2O$, is precipitated by an excess of sodium chloride. The *nitrate*, $\left[\begin{matrix}(OAc)_6\\ Cr_3\ 3Py\\ (OH)_2\end{matrix}\right]NO_3,5H_2O$, is very sparingly soluble, one part dissolving in 216·9 parts of water. The *nitrate-acetate*, $\left[\begin{matrix}(OAc)_6\\ 3Py\\ Cr_3\ OH_2\\ OH\end{matrix}\right]\begin{matrix}NO_3\\ OAc\end{matrix},3H_2O$; the *platinichloride*, $\left[\begin{matrix}(OAc)_6\\ Cr_3\ 3Py\\ (OH)_2\end{matrix}\right]\frac{1}{2}PtCl_6$; the *stannichloride*, $\left[\begin{matrix}(OAc)_6\\ 3Py\\ Cr_3\ OH_2\\ OH\end{matrix}\right]SnCl_6,7H_2O$; the *permanganate*, $\left[\begin{matrix}(OAc)_6\\ Cr_3\ 3Py\\ (OH)_2\end{matrix}\right]MnO_4.H_2O$; the *ferricyanide*,

$$\left[\begin{matrix}(OAc)_6\\ Cr_3\ 3Py\\ (OH)_2\end{matrix}\right]Fe(CN)_6,9H_2O,$$

and the *chromate* have been analysed. A number of other salts are briefly described.

[With E. Büttner]—Ammonia may also be introduced, by passing the gas into an alcoholic solution of hexa-acetatotrichromic diacetate. The sparingly soluble *hexa-acetatotriammine-trichromic iodide*,

$$\left[\begin{matrix}(OAc)_6\\ Cr_3\ 3NH_3\\ (OH)_2\end{matrix}\right]I,$$

resembles the pyridine compound. C. H. D.

Course of the Friedel-Craft Reaction with Unsymmetrical Polycarboxylic Acids. II. Alfred Kirpal (*Monatsh.*, 1910, 31, 295—299. Compare Abstr., 1909, i, 509).—Unlike the case of

cinchomeronic anhydride (*loc. cit.*), the addition of benzene to quinolinic anhydride in the presence of aluminium chloride yields only one product, namely, 3-benzoylpicolinic acid in 92% yield. The other product, *2-benzoylnicotinic acid*, $C_5NH_3Bz\cdot CO_2H$, m. p. 176°, which is not formed or only in inappreciable amount in the preceding reaction, can be prepared from benzene, 3-methyl quinolinate-2-chloride and aluminium chloride. C. S.

New Trimethylenepyrrole Derivatives. II. Mario Ghiglieno (*Atti. R. Accad. Sci. Torino*, 1910, 45, 449—468).—The hydrolysis of the *α*- and *β*-forms of 3 : 5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (compare this vol., i, 427) by 2 or more mols. of sodium hydroxide in dilute solution at the ordinary temperature consists of a reaction with $3H_2O$, two isomeric mono-amides of 3 : 5-dicarboxy-4-methyl-4-ethyltrimethylenedicarbonimides,

$$NH<\begin{matrix}CO\cdot C(CO\cdot NH_2)\\ |\\ CO\cdot C(CO_2H)\end{matrix}>CMeEt,$$

being obtained.

The complete hydrolysis of the second cyanogen group to carboxyl is accomplished only with difficulty. It is hence evident that tertiary nitriles, which are usually regarded as hydrolysable with difficulty, can be very easily hydrolysed in certain cases. The influence of alkyl groups or negative radicles in hindering the hydrolysis of the cyanogen group is not general, or at any rate varies considerably according to the nature of the fundamental nucleus. The iminic group is perhaps more resistant to the action of alkali than is generally believed, and in some cases may exhibit very marked stability. Whilst the iminic hydrogen possesses a very feeble acid character when the neighbouring atoms or groups are neutral or nearly so, this character seems to be influenced regularly by the introduction of more active substituent groups, being increased by highly electronegative groups like cyanogen, and diminished to the vanishing point by the proximity of one or more acid groups.

The *α-amide*, $C_{10}H_{12}O_5N_2$, prepared from *α*-3 : 5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (m. p. 247—248°), forms colourless, rhombic prisms, m. p. 194° (decomp.) or 232—235° (Maquenne block). It behaves as a dibasic acid weaker than phenolphthalein ; the *ammonium hydrogen*, *sodium*, and *silver* ($C_{10}H_{10}O_5N_2Ag_2,2H_2O$) salts were prepared.

The *β*-isomeride, $C_{10}H_{12}O_5N_2$, prepared from the corresponding trimethylenedicarbonimide derivative, forms shining crystals, m. p. 206° (decomp.), decomposes instantaneously on the Maquenne block at 280°. The *silver* salt, $C_{10}H_{10}O_5N_2Ag_2,2H_2O$, was prepared.

The *amide* of *3-carboxy-4-methyl-4-ethyltrimethylenedicarbonimide*, $NH<\begin{matrix}CO\cdot CH\\ |\\ CO\cdot C(CONH_2)\end{matrix}>CMeEt$, prepared by heating the *α*-mono-amide of the dicarboxy-acid (m. p. 194°) at 165—170°, forms shining crystals, m. p. 141—143° or 142—143° (Maquenne block), and has a feeble acidic character ; its *silver* salt, $C_9H_{11}O_5N_2Ag$, was analysed.

The *α-dicarboxy-acid*, $NH<\begin{matrix}CO\cdot C(CO_2H)\\ |\\ CO\cdot C(CO_2H)\end{matrix}>CMeEt$, forms small, white

needles ($+2H_2O$), decomposing instantaneously on the Maquenne block at 182—183°, and is dibasic towards phenolphthalein, being the only compound of the series in which the iminic hydrogen of the pyrrole ring exhibits no acid reaction; the *sodium hydrogen* salt was analysed and various other salts prepared.

α-4-Methyl-4-ethyltrimethylenedicarbonimide, $NH<\begin{matrix}CO\cdot CH\\ |\\ CO\cdot CH\end{matrix}>CMeEt$,

prepared by heating the above dicarboxy-acid, forms slender, nacreous laminæ, m. p. 61—63°, and exhibits extremely feeble acid properties; when its solution is neutralised, it gives precipitates with salts of the heavy metals. T. H. P.

Dihydro*iso*indole Bases. Julius von Braun (*Ber.*, 1910, 43, 1353—1360. Compare Abstr., 1907, i, 960; 1909, i, 507).—A tertiary dihydro*iso*indole, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>NR$, was sought in which the alkyl residue R, in presence of cyanogen bromide, was less firmly attached to nitrogen than the xylyl residue of the ring. This xylyl residue is found to take up a position between benzyl and methyl in its attachment to nitrogen; accordingly in the case of *N*-methyl- and *N*-ethyldihydro*iso*indoles the ring is opened by cyanogen bromide. *N*-Benzyldihydro*iso*indole under the same conditions has the benzyl eliminated to some extent. *N*-Allyldihydro*iso*indole is transformed into *N*-cyanodihydro*iso*indole.

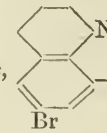
o-Xylylmethylaniline, prepared by the interaction of methylaniline and *o*-xylyl bromide, forms a clear liquid, b. p. 200°/35 mm., m. p. 34°; the picrate has m. p. 110°. It interacts with cyanogen bromide in sealed tubes at 100°, forming a mixture of phenyl-*o*-xylylcyanide, phenylmethylcyanamide, and ω-bromo-*o*-xylene.

Benzyldihydro*iso*indole is a colourless oil, b. p. 185—186°/10 mm.; it reacts with cyanogen bromide, forming the *quaternary ammonium bromide*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N(C_7H_7)_2Br$, m. p. 220°. It also in part decomposes into benzyl bromide and *N-cyanodihydroisoindole*.

*Allyldihydro*iso*indole*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot C_3H_5$, prepared by the reaction of xylylene bromide and allylamine in chloroform solution, has b. p. 125°/17 mm. It forms an oily *picrate* and a methiodide, m. p. 131°. It reacts very energetically with cyanogen bromide, forming allylbromide and *cyanodihydroisoindole*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot CN$, which forms colourless crystals, m. p. 80—81°. Boiling for a short time with 25% sulphuric acid converts it into *dihydroisoindolecarboxylamide*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot CO\cdot NH_2$, m. p. 183°. Further hydrolysis yields dihydro*iso*indole, b. p. 213—214°, previously prepared synthetically by Gabriel (Abstr., 1893, i, 347). E. F. A.

Derivatives of Tetrahydroquinoline. II. Franz Kunckell [with W. Theopold] (*Ber. deut. pharm. Ges.*, 1910, 20, 214—225).—The work described in the first part of this research (this vol., i, 429) is continued, bromomethyltetrahydroquiniminazole, dibromotetrahydroquino-

line, dibromoquinoline, and some of their derivatives being described. It has been pointed out already (*loc. cit.*) that the end product of the reduction of 6-bromo-8-nitro-1-acetyltetrahydroquinoline is a bromoanhydro-base of the class that Bamberger and Wulz have called "quiniminazoles" (*peri*-quinolineazoles) (Abstr., 1891, i, 1255). The reduction can be effected by tin and hydrochloric acid, as described already, or by means of zinc dust and acetic acid.

2-Methyl-8-bromotetrahydroquinolineazole,  , m. p. 165°,

separates from light petroleum in colourless crystals, and shows none of the characteristic properties of a tetrahydroquinoline derivative. The *hydrochloride*, m. p. 253°, obtained by the action of hydrogen chloride on an ethereal solution of the base, crystallises in faintly yellow needles. The *platinichloride*, m. p. above 300°, is a brown, amorphous product.

On bromination in acetic acid, tetrahydroquinoline furnishes 5 : 7-dibromotetrahydroquinoline hydrobromide, m. p. 185°, which forms colourless crystals, and on addition of alkali to its solution in warm water yields the dibromo-base as a yellow, non-volatile oil. The hydrochloride, m. p. 178°, forms colourless crystals, and the platinichloride, m. p. 210° (decomp.), crystallises in small, brown needles. This dibromotetrahydroquinoline is probably identical with that of Hoffmann and Königs (Abstr., 1883, 1145).

5 : 7-*Dibromo*-8-*nitroquinoline*, m. p. 180°, prepared from 8-nitroquinoline (Knüppel, Abstr., 1896, i, 391) by heating it at 130° with water and bromine (2 mols.), crystallises from alcohol in minute, almost colourless needles. It cannot be further nitrated, and the bromine atoms are not reactive. The substance is scarcely basic, but although it forms no hydrochloride, a brown, microcrystalline *platinichloride*, m. p. 265° (decomp.), can be obtained by adding platinum chloride solution, saturated with hydrogen chloride, to a solution of the substance in alcohol, also saturated with hydrogen chloride. On heating at 230° with alcohol, saturated with ammonia at 0°, 5 : 7-dibromo-8-nitroquinoline is converted into the corresponding dibromoaminoquinoline, m. p. 127°, already obtained by Claus and Ammelburg (Abstr., 1894, i, 553). The *acetyl* derivative of this has m. p. 172°, and the *benzoyl* derivative, m. p. 155—156°. 5-*Bromo*-8-*nitro*-6-*methylquinoline*, m. p. 185—186°, prepared by heating 8-nitro-6-methylquinoline (Knüppel, Abstr., 1896, i, 391) with bromine in a closed tube at 130°, forms small, colourless crystals from a mixture of alcohol, ether, and benzene. It does not furnish a hydrochloride, but gives a *platinichloride* ; the bromine atom is not attacked by aqueous or alcoholic alkali at 250°.

T. A. H.

Derivatives of Benzothiazole. Emil Besthorn (*Ber.*, 1910, 43, 1519—1526).—1-Imino-2-methylbenzothiazoline,

$$C_6H_4\!<\!\overset{NMe}{S}\!>\!C{:}NH$$

(Hugershoff, Abstr., 1903, i, 866), obtained by the action of bromine on a chloroform solution of *as*-phenylmethylthiocarbamide, is identical with

Fischer and Besthorn's phenylmethylthiocarbizine. With nitrous acid it yields a *nitroso*-derivative, $C_6H_4<^{NMe}_{S}>C{:}N{\cdot}NO$, which crystallises in slender, yellow needles or compact, red crystals. When gently heated, it decomposes at about 147°, but when heated rapidly explodes at 152°. It reacts with concentrated hydrochloric acid, yielding nitrous fumes, and when its xylene solution is boiled, nitrogen is evolved and 2-*methylbenzothiazolone*, $C_6H_4<^{NMe}_{S}>CO$, is formed. This compound crystallises from ether in compact prisms, m. p. 76°, and yields salts with concentrated mineral acids. It is decomposed when boiled with alcoholic potassium hydroxide solution, and does not yield a phenylhydrazone.

2-*Methylbenzothiazolonehydrazone*, $C_6H_4<^{NMe}_{S}>C{:}N{\cdot}NH_2$, obtained by reducing the nitroso-derivative with zinc dust and acetic acid at 15°, crystallises in colourless, thin plates, m. p. 143—144°, and has very feeble reducing properties at the ordinary temperature. Its *hydrochloride* is sparingly soluble in concentrated hydrochloric acid. The *benzylidene* derivative, $C_6H_4<^{NMe}_{S}>C{:}N{\cdot}N{:}CHPh$, forms pale yellow plates, m. p. 163°, has but feebly basic properties, and gives a characteristic blue coloration with ferric chloride and a few drops of hydrochloric acid in aqueous alcoholic solution. J. J. S.

Action of Alkalis on Aromatic Acid Hydrazides. Theodor Curtius and Heinrich Melsbach [and, in part, Rissom] (*J. pr. Chem.*, 1910, [ii], 81, 501—551).—Curtius observed (Abstr., 1900, i, 701) that the action of dilute alkali on dextrose and benzoylhydrazine in aqueous solution at the ordinary temperature produced, not benzosazones, but benzoylbenzylidene hydrazine, the dextrose apparently playing no part in the reaction. The authors have now examined the reaction fully. A known quantity (about 3 mols.) of benzoylhydrazine is dissolved in a measured volume of water, and a definite amount of sodium hydroxide (1 mol.) is added; after a definite interval of time, the precipitated benzoylbenzylidenehydrazine is collected and weighed, its purity being checked by hydrolysing it by dilute sulphuric acid, distilling the benzaldehyde with steam into a solution of hydrazine sulphate, and collecting and weighing the benzylideneazine produced.

It is found that the presence of a small quantity of dextrose increases the yield of benzoylbenzylidenehydrazine; by increasing the amount of dextrose, the yield of the hydrazide is diminished. At 70° the yield of benzoylbenzylidenehydrazine is considerably less than at 40°, or at the ordinary temperature, but again the presence of dextrose exercises a favourable influence on the yield. When the amount of sodium hydroxide is increased to 3 mols., the authors find that in experiments in which dextrose is present the product during the first four weeks is benzoylbenzylidenehydrazine, and during the next four weeks, benzylideneazine; when dextrose is not present, the only product is the azine.

The conversion of benzoylhydrazine into benzoylbenzylidenehydrazine also occurs in the presence of ammonium hydroxide, or, very slowly, in

that of hydrazine hydrate. The change also takes place in alcoholic solution; in this solvent the best yield, 47·9%, of benzoylbenzylidenehydrazine is obtained; the rest of the benzoylhydrazine suffers hydrolysis, benzoic acid being produced.

The reaction is explained by the elimination of hydrazine from two molecules of benzoylhydrazine, which reduces one of the resulting residues, whereby benzoylbenzylidenehydrazine is formed:

$$2NHBz\cdot NH_2 \longrightarrow N_2H_4 + 2\cdot NHBz \longrightarrow$$
$$\cdot NHBz + \cdot N{:}CHPh \longrightarrow NHBz\cdot N{:}CHPh.$$

The hydrolysis of the last by water (2 mols.) yields benzoic acid, benzaldehyde, and hydrazine, from the last two of which benzylideneazine is produced.

The reaction represented by the scheme:

$$C_6H_4R\cdot CO\cdot NH\cdot NH_2 \longrightarrow C_6H_4R\cdot CO\cdot NH\cdot N{:}CH\cdot C_6H_4R$$

has been examined in the case of other aromatic acid hydrazides. It is found that in aqueous or alcoholic solution in the presence of sodium hydroxide the conversion takes place when R is *m*-NO_2 *m*-Cl, *p*-Br, *p*-Me, *o*-NH_2, *o*-OH, or *p*-OMe, but not when R is *o*-NO_2 or *p*-NO_2.

The following new compounds are described: o-*Nitrobenzoyl*-o-*nitrobenzylidenehydrazine*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2$, m. p. 215°; the para-*isomeride*, m. p. 274°; the meta-*isomeride*, m. p. 248°; p-*bromobenzoyl*-p-*bromobenzylidenehydrazine*, m. p. 232—233°; p-*bromobenzylideneazine*, m. p. 209·5—210°; m-*chlorobenzoyl*-m-*chlorobenzylidenehydrazine*, m. p. 147—148°; m-*chlorobenzylideneazine*, m. p. 143—144°: o-*aminobenzoyl*-o-*aminobenzylidenehydrazine*, m. p. 188—189°; o-*hydroxybenzoyl*-o-*hydroxybenzylidenehydrazine*, m. p. 277°; *anisoylhydrazine*, m. p. 136°; *anisoylanisylidenehydrazine*, m. p. 171°. C. S.

Relations between Constitution and Phototropy. Maurice Padoa and F. Graziani (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 489—495).—The relationship between constitution and phototropy observed with the tolyl- and naphthyl-hydrazones (Abstr., 1909, i, 964; this vol., i, 135) is found to hold also with the xylylhydrazones; thus, the xylylhydrazine in which $Me:Me:N_2H_3 = 1:3:4$ yields non-phototropic hydrazones, whilst when $Me:Me:N_2H_3 = 1:2:4$ the hydrazones are, in nearly all cases, phototropic.

Benzaldehyde-1:3:4-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CHPh$, forms shining, yellow scales, m. p. 86°, undergoes alteration in the air, and is not phototropic.

Anisaldehyde-1:3:4-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4\cdot OMe$, forms slender, yellow needles, m. p. 97°, changes in the air, and does not exhibit phototropy.

Cinnamaldehyde-1:3:4-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot CH{:}CHPh$, forms lemon-yellow, non-phototropic crystals, m. p. 115°.

Cuminaldehyde-1:3:4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4\cdot CHMe_2,$$

forms white needles, m. p. 76°, and is not phototropic.

Piperonaldehyde-1:3:4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_3{:}O_2{:}CH_2,$$

forms faintly red, non-phototropic crystals, m. p. 90°.

p-*Tolualdehyde*-1 : 3 : 4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4Me,$$

forms canary-yellow crystals, m. p. 99°, and is not phototropic.

Vanillin-1 : 3 : 4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_3(OH)\cdot OMe,$$

crystallises in slender, yellow, non-phototropic crystals, m. p. 99°.

Salicylaldehyde-1 : 3 : 4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4\cdot OH,$$

forms yellow needles, m. p. 86°, and is non-phototropic.

1 : 2 : 4-*Xylylhydrazine*, $NH_2\cdot NH\cdot C_6H_3Me_2$, forms yellowish-white needles, m. p. 57°, and its *hydrochloride*, shining, white scales, m. p. 197° (decomp.).

Benzaldehyde-1 : 2 : 4-*xylylhydrazone* forms a faintly yellow, crystalline powder, m. p. 126°, and exhibits phototropy.

Anisaldehyde-1 : 2 : 4-*xylylhydrazone* crystallises in white, phototropic needles, m. p. 116°.

Cinnamaldehyde-1 : 2 : 4-*xylylhydrazone* forms yellow needles, m. p. 153°, and is non-phototropic.

Cuminaldehyde-1 : 2 : 4-*xylylhydrazone* forms slender, yellow needles, m. p. 143°, and exhibits phototropy.

Piperonaldehyde-1 : 2 : 4-*xylylhydrazone* crystallises as a white, phototropic powder, m. p. 118°.

p-*Tolualdehyde*-1 : 2 : 4-*xylylhydrazone* forms a canary-yellow, crystalline powder, m. p. 135°, and is phototropic.

Vanillin-1 : 2 : 4-*xylylhydrazone* forms a white, crystalline, non-phototropic powder, m. p. 118°.

Salicylaldehyde-1 : 2 : 4-*xylylhydrazone* forms yellowish, faintly phototropic needles, m. p. 157°.

Piperonaldehyde-β-naphthylhydrazone (compare Rothenfusser, Abstr., 1908, i, 52) and vanillin-β-naphthylhydrazone, m. p. 185° (Rothenfusser, *loc. cit.*, gave 187°) are phototropic.

p-*Tolualdehyde* - β - *naphthylhydrazone*, $C_{10}H_7\cdot N_2H{:}CH\cdot C_6H_4Me$, crystallises in faintly yellow, phototropic scales, m. p. 188°.

Salicylaldehyde - β - *naphthylhydrazone*, $C_{10}H_7\cdot N_2H{:}CH\cdot C_6H_4\cdot OH$, forms dirty-yellow needles, m. p. 187°, and is non-phototropic.

T. H. P.

Isatinanils. II. Derivatives of Thionaphthenquinone. Rudolf Pummerer (*Ber.*, 1910, 43, 1370—1376. Compare this vol., i, 77).—The methylene group of 3-hydroxy-1-thionaphthen reacts even more smoothly than that of indoxyl with alcoholic solutions of aromatic nitroso-compounds in the presence of sodium hydroxide, thionaphthenquinone-2-anils being formed in good yield, together with a very small amount of "thioindigo." In this way thionaphthenquinone-2-anil is obtained from nitrosobenzene ; *thionaphthenquinone*-p-*dimethylamino*-2-*anil*, $C_6H_4<^{-S-}_{CO}>C{:}N\cdot C_6H_4\cdot NMe_2$, m. p. 176°, from *p*-nitrosodimethylaniline ; 5-*methylthionaphthenquinone*-p-*dimethylamino*-2-*anil*, m. p. 200°, from 3-hydroxy-5-methyl-1-thionaphthen ; 5-*chlorothionaphthenquinone*-p-*dimethylamino*-2-*anil*, m. p. 148—149°, and 7-*chlorothionaphthenquinone*-p-*dimethylamino*-2-*anil*, m. p. 147°, from the corre-

sponding chlorinated hydroxythionaphthens; and *thionaphthenquinone-p-phenylamino-2-anil*, m. p. 193°, from *p*-nitrosodiphenylamine.

The anil group in these compounds is very loosely held. They are decomposed by mineral acids, yielding the corresponding thionaphthenquinones, and react with substances containing a reactive methylene group, such as indoxyl, oxindole, 3-hydroxy-1-thionaphthen, or acenaphthenone, forming an indigoid dye, the anil group being eliminated as arylamine.

The salts of these anils are of interest. Isatin-*p*-dimethylamino-2-anil forms a hydrate, a yellow hydrochloride, and also an isomeric blue hydrochloride (*loc. cit.*). The latter salt may be quinonoid, but in any explanation of the isomerism a possible migration of the indole-iminic hydrogen atom must not be overlooked. Such a contingency is impossible in the case of the thionaphthenquinoneanils. Thionaphthenquinone-*p*-dimethylamino-2-anil forms a yellow *hydrochloride*, but no hydrate, whilst thionaphthenquinone-*p*-phenylamino-2-anil forms a green *hydrate*, containing H_2O, and a hydrated blue *hydrochloride*, $C_{20}H_{14}ON_2S,1\frac{1}{2}HCl,1\frac{1}{2}H_2O$, decomposing at 120°. These facts alone do not elucidate the constitution of the blue salts, but it is noteworthy that the formation of blue salts runs pari passu with hydrate formation.

Thionaphthenquinone-2-oxime also is hydrolysed by boiling strong mineral acids, yielding thionaphthenquinone, and reacts with indoxyl in dilute acetic or weak mineral acid solution forming indigotin and 2′-indoxyl-2-thionaphthen-2′-one. C. S.

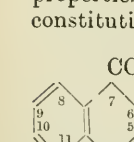
Isatinanils. III. Leuco-compounds. Rudolf Pummerer and Maximilian Göttler (*Ber.*, 1910, **43**, 1376—1386. Compare preceding abstract).—*Isatin-leuco-3-anil*, $C_{14}H_{12}ON_2$, m. p. 192° in an atmosphere of carbon dioxide, is obtained by reducing isatin-3-anil in 2% sodium hydroxide by sodium hyposulphite and liberating the leucoanil by sodium hydrogen carbonate in an atmosphere of coal gas. It separates from benzene in colourless prisms.

Isatin-leuco-2-anil, $C_6H_4<^{CO}_{NH}>CH\cdot NHPh$, m. p. 115—116°, is prepared by reducing an alcoholic solution of isatin-2-anil by a solution of sodium hyposulphite in 4% sodium hydroxide and alcohol in an atmosphere of coal gas, and decomposing the product by sodium hydrogen carbonate; it crystallises in citron-yellow prisms, and oxidises to the anil with extreme readiness. *Isatin-*p*-dimethylamino-leuco-2-anil*, $C_{16}H_{17}ON_2$, m. p. 150—155°, obtained in a similar manner, is colourless, and is less readily oxidised than the preceding anil. Isatin-leuco-2-anil behaves in a remarkable manner with acids, concentrated sulphuric acid, dilute hydrochloric acid, hot or cold, acetic acid, or even a 1·5% boiling solution of benzoic acid, causing two simultaneous reactions, by one of which aniline and indigotin are produced, whilst the other results in the formation of aniline, water, and indirubin-2-anil. Isatin-leuco-2-anil is reduced extremely slowly by alkaline sodium hyposulphite, fairly rapidly to indoxyl by cold ammonium sulphide, and instantly to indigotin by warm ammonium sulphide in an atmosphere of carbon dioxide. Isatin-2-anil, however,

is instantly reduced to indoxyl by ammonium sulphide at 0° in an atmosphere of carbon dioxide.

Indirubin-2-anil, $C_6H_4<\begin{matrix}NH\\CO\end{matrix}>C:C<\begin{matrix}-C_6H_4-\\C(:NPh)\end{matrix}>NH$, m. p. 219—220°, can be obtained by the interaction of isatin-leuco-2-anil and a hot alkaline solution of indoxyl (indoxylic acid), but is best prepared by slowly adding a hot alcoholic solution of isatin-2-anil to a hot aqueous-alcoholic alkaline (0·5% sodium hydroxide) solution of indoxylic acid in an atmosphere of coal gas. It separates from benzene in metallic, violet plates containing C_6H_6, forms a blue *hydrochloride*, $C_{22}H_{15}ON_3,CHl$, m. p. 245°, and yields isatin and isatin-2-anil by oxidation by potassium permanganate in glacial acetic acid. C. S.

Anhydrides of 1-Phenyl-5- and -*o*-3-pyrazolonecarboxylic Acids. August Michaelis (*Annalen*, 1910, 373, 129—212).—The present communication contains an account of the preparation and properties of several derivatives of a compound having the annexed constitution, which it is proposed to designate pyrazo*iso*coumarazone,



since it is formed by the union of a pyrazole ring with the *iso*coumarazone nucleus (compare Cebrian, Abstr., 1898, i, 582); the anhydride of 1-phenyl-3-methyl-5-pyrazolone-2′-carboxylic acid, formed by the elimination of hydrogen chloride from 5-chloro-1-phenyl-3-methylpyrazole-2′-carboxylic acid (compare Michaelis and Eisenschmidt, Abstr., 1904, i, 624), is to be regarded, therefore, as 3-methylpyrazo*iso*coumarazone. This compound has been isolated in three isomeric modifications; the γ-isomeride is formed by the distillation of 5-chloro-1-phenyl-3-methylpyrazole-2′-carboxylic acid, and passes into the α-isomeride when heated with zinc chloride or water for some time, and into the β-isomeride when acted on by nitric or sulphuric acid or when distilled under the atmospheric pressure. 1-Phenyl-3-methyl-5-pyrazolone-2′-carboxylic acid is obtained when hydrochloric acid is added to a solution of any one of the isomerides in alkali; similarly, the same salt, $C_{11}H_8O_2N_2,HCl,H_2O$, is formed by heating the three modifications with an excess of hydrochloric acid, yet the isomerism is not merely physical, since three isomeric 4-bromo-derivatives are formed by acting on the isomerides with bromine in glacial acetic acid.

The β-isomeride has also been prepared by the condensation of ethyl acetoacetate with *o*-hydrazinobenzoic acid.

The parent substance, namely, pyrazo*iso*coumarazone, has been similarly prepared from 5-chloro-1-phenylpyrazole-2′-carboxylic acid, also the 3-phenyl derivative from 5-chloro-1 : 3-diphenylpyrazole-2′-carboxylic acid, and by the condensation of ethyl benzoylacetate with *o*-hydrazinobenzoic acid; isomeric forms of these compounds have not been isolated. The pyrazo*iso*coumarazones resemble *iso*coumarin and phthalic anhydride in their general chemical behaviour.

3-Chloro-1-phenyl-5-methylpyrazole-2′-carboxylic acid, when heated, also loses hydrogen chloride, yielding methylbenzo*bis*pyrazolone, $\begin{matrix}C_6H_4\cdot N\cdot CMe\\|\quad\quad|\\CO---N\cdot CO\end{matrix}>CH$ (compare Michaelis and Reinighaus, Abstr., 1909,

i, 530), but the halogen of 4-bromo-1-phenyl-3-methylpyrazole-2′-carboxylic acid is not eliminated as hydrogen bromide by heating the acid.

[With Max Ziesel.]—*Ethyl* o-*tolylhydrazinomethylenemalonate*, $C_6H_4Me\cdot NH\cdot NH\cdot CH:C(CO_2Et)_2$, is prepared by the interaction of *o*-tolylhydrazine with ethyl ethoxymethylenemalonate; it forms colourless, rhombic plates and prisms, m. p. 110°, and is converted by aqueous sodium hydroxide into 1-o-*tolyl*-5-*pyrazolone*, $C_{10}H_{10}ON_2$, which crystallises in colourless prisms and plates, m. p. 177°, and when heated with phosphorus oxychloride yields 5-*chloro*-1-o-*tolylpyrazole*, $C_{10}H_9N_2Cl$, a colourless liquid with a characteristic odour; the latter substance, when oxidised with chromic acid, yields 5-*chloro*-1-*phenylpyrazole*-2′-*carboxylic acid*, $C_{10}H_7O_2N_2Cl$, which crystallises in long, colourless needles, m. p. 125°, and on distillation yields *pyrazoisocoumarazone*, colourless needles, m. p. 116°, b. p. 308°. The latter substance is converted (1) by bromine into 4-*bromopyrazoisocoumarazone*, $C_{10}H_5O_2N_2Br$, slender, colourless needles, m. p. 199°, and (2) by aqueous ammonia under pressure at 120° into 7-*hydroxypyrazoquinazoline*, $OH\cdot C\begin{matrix}N-\!\!-C:CH\\ \vert\quad\quad\vert\\ C_6H_4\cdot N-\!\!-N\end{matrix}>CH$, which forms small, colourless needles, m. p. 265°, and is converted by phosphoryl chloride into 7-*chloropyrazoquinazoline*, $C_{10}H_6N_3Cl$, pale yellow needles, m. p. 130°.

[With Carl Krug, Julius Leo, and Max Ziesel.]—The o-*carboxyphenylhydrazone* of ethyl acetoacetate,

$$CO_2Et\cdot CH_2\cdot CMe:N\cdot NH\cdot C_6H_4\cdot CO_2H,$$

prepared by the action of *o*-hydrazinobenzoic acid on ethyl acetoacetate, forms slender, yellow needles, m. p. 125°, and is converted when distilled (1) under a pressure of 15 mm. into *β*-3-*methylpyrazoisocoumarazone*, white needles, m. p. 132°, and (2) under the atmospheric pressure into γ-3-*methylpyrazoisocoumarazone*, white needles, m. p. 112°, b. p. 345°; *α*-3-*methylpyrazoisocoumarazone* crystallises in white needles, m. p. 165°. The isomeric 3-methylpyrazo*iso*coumarazones, when acted on by a solution of bromine in glacial acetic acid, yield the corresponding 4-*bromo*-3-*methylpyrazoisocoumarazones*, $C_{11}H_7O_2N_2Br$; the *α*-compound forms yellow needles, m. p. 187°; the *β*-isomeride crystallises in colourless needles, m. p. 151°; the γ-modification forms colourless needles, m. p. 135—137°, and is converted by repeated crystallisation from alcohol into the *β*-isomeride. The *β*- and γ-isomeric forms of 3-methylpyrazo*iso*coumarazone, when treated with iodine in glacial acetic acid, yield γ-4-*iodo*-3-*methylpyrazoisocoumarazone*, $C_{11}H_7O_2N_2I$, colourless, silky needles, m. p. 182°; the *α*-isomeride is not acted on by iodine in glacial acetic acid, but in the presence of iodic acid yields *α*-4-*iodo*-3-*methylpyrazoisocoumarazone*, greenish-yellow needles, m. p. 198°.

3-Methylpyrazo*iso*coumarazone is converted by aqueous-alcoholic ammonia under pressure at 130° into 7-*hydroxy*-3-*methylpyrazoquinazoline*, $C_{11}H_9ON_3$, long, white needles, m. p. 275—276°; the *silver* salt, $C_{11}H_8ON_3Ag$, forms small, white needles; the *chloro*-derivative, $CMe\begin{matrix}N-\!\!-N\cdot C_6H_4\\ \vert\quad\quad\vert\\ CH:C-\!\!-NCl\end{matrix}>CO$, formed by the action of calcium hypochlorite

on a solution of the quinazoline in aqueous alkali, crystallises in small, red needles, m. p. 275°. 7-Hydroxy-3-methylpyrazoquinazoline is converted (1) by phosphorus oxychloride into *7-chloro-3-methylpyrazoquinazoline*, $C_{11}H_8N_3Cl$, which crystallises in glistening, yellow needles, m. p. 139°, and when treated with an alcoholic solution of sodium ethoxide yields *7-ethoxy-3-methylpyrazoquinazoline*, $C_{13}H_{13}ON_3$, glistening, white, felted needles, m. p. 125°, and (2) by phosphorus pentachloride into *4 : 7-dichloro-3-methylpyrazoquinazoline*, $C_{11}H_7N_3Cl_2$, crystallising in glistening, yellow needles, m. p. 174—175°.

3-Methyl-6-ethyldihydropyrazoquinazolone,

$$CMe\begin{matrix}\diagup N—N\cdot C_6H_4 \\ \diagdown CH{:}C\text{–}NEt\end{matrix}\diagup CO,$$

is prepared by the action of ethylamine on methylpyrazo*iso*coumarazone; it forms glistening, pale yellow needles, m. p. 133—134°; the corresponding 6-*phenyl* compound, $C_{17}H_{13}ON_3$, similarly prepared by using aniline, crystallises in colourless needles, m. p. 156°; the corresponding 6-*anilino*-compound, $C_{17}H_{14}ON_4$, obtained by using phenylhydrazine, forms lemon-yellow leaflets, m. p. 195°; the corresponding 6-*amino*-compound, $CMe\begin{matrix}\diagup N—N\cdot C_6H_4— \\ \diagdown CH{:}C\cdot N(NH_2)\end{matrix}\diagup CO$, prepared by heating methylpyrazo*iso*coumarazone with hydrazine hydrate at 180°, crystallises in colourless needles, m. p. 249°, and condenses with benzaldehyde and benzophenone, yielding the *benzylidene* derivative, $C_{11}H_8ON_3\cdot N{:}CHPh$, white needles, m. p. 174°, and *diphenylmethylene* derivative, $C_{11}H_8ON_3\cdot N{:}CPh_2$, white needles, m. p. 257° respectively; the corresponding *carbamide*,

$$C_{11}H_8ON_3\cdot NH\cdot CO\cdot NH_2,$$

prepared by the action of semicarbazide on methylpyrazo*iso*coumarazone, crystallises in needles, m. p. 265°.

4-Bromo-1-phenyl-3-methyl-5-pyrazolone-2′-carboxylic acid,

$$C_{11}H_9O_3N_2Br,$$

is formed by the action of aqueous sodium hydroxide on either of the 4-bromo-3-methylpyrazo*iso*coumarazones; it forms colourless needles, m. p. 202°.

1-Phenyl-3-methyl-5-pyrazolone-2′-carboxylic acid,

$$\begin{matrix}CH_2\cdot CO \\ CMe{=}N\end{matrix}\diagup N\cdot C_6H_4\cdot CO_2H,$$

similarly prepared from the methylpyrazo*iso*coumarazones, forms slightly yellow crystals, m. p. 195°; the 4-*oximino*-derivative,

$$C_{11}H_9O_4N_3,$$

crystallises with $1H_2O$ in rosettes of yellow needles, m. p. 139°; the anhydrous substance has m. p. 200°; the 4-*benzylidene* derivative, $C_{18}H_{14}O_3N_2$, forms white crystals, m. p. 243°; the 4-*benzeneazo*-derivative, $C_{17}H_{14}O_3N_4$, crystallises in golden-yellow needles, m. p. 205°.

[With Julius Leo.]—The following compounds are prepared by methods similar to those employed in the preparation of the corresponding compounds just described: 1-o-*tolyl*-3 : 4-*dimethyl*-5-*pyrazolone*, $C_{12}H_{14}ON_2$, forms white needles, m. p. 179°; 5-*chloro*-1-o-*tolyl*-3 : 4-*dimethylpyrazole*, $C_{12}H_{13}N_2Cl$, is a white, crystalline mass, m. p. 48°;

the *methiodide*, $C_{12}H_{13}N_2Cl,MeI$, forms white, silky, felted needles, m. p. 187°; *5-chloro-1-phenyl-3-methylpyrazole-4 : 2'-dicarboxylic acid*, $C_{12}H_9O_4N_2Cl$, crystallises in slender, white needles, m. p 226° (decomp.); the latter substance yields 3-methylpyrazo*iso*coumarazone when distilled under a pressure of 16 mm. at 201°, and *3-methylpyrazo-isocoumarazone-4-carboxylic acid*, $C_{12}H_8O_4N_2$, slightly yellow, slender needles, m. p. 224° (decomp.), when heated at 171° under a pressure of 16 mm.; *3-phenyl-1-o-tolyl-5-pyrazolone*, $C_{16}H_{14}ON_2$, crystallises in glistening, white leaflets, m. p. 191°; *5-chloro-3-phenyl-1-o-tolylpyrazole*, $C_{16}H_{13}N_2Cl$, is a white, crystalline mass, m. p. 46°; *5-chloro-1 : 3-diphenylpyrazole-2'-carboxylic acid*, $C_{16}H_{11}O_2N_2Cl$, crystallises with $1H_2O$ in stout, white prisms, m. p. 239° (decomp.); *ethyl benzoylacetate o-carboxyphenylhydrazone*, $CO_2Et{\cdot}CH_2{\cdot}CPh{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, forms slender, yellow needles, m. p. 166—167°; *3-phenylpyrazoisocoumarazone*, $C_{16}H_{10}O_2N_2$, crystallises in glistening, slender, white needles, m. p. 199°; *4-bromo-3-phenylpyrazoisocoumarazone*, $C_{16}H_9O_2N_2Br$, forms glistening, white needles, m. p. 187°; the corresponding *4-chloro*-compound crystallises in slender, white needles, m. p. 170°; *7-hydroxy-3-phenylpyrazoquinazoline*, $C_{16}H_{11}ON_3$, crystallises in felted, white needles, m. p. 315°; the crystalline *potassium* and *silver* salts were analysed; *4 : 6-dichloro-3-phenyldihydropyrazoquinazolone*, $C_{16}H_9ON_3Cl$, forms slender, silky, yellow needles, m. p. 243—248°; *7-chloro-3-phenylpyrazoquinazoline*, $C_{16}H_{10}N_3Cl$, crystallises in glistening, slightly yellow needles, m. p. 145°; *4 : 7-dichloro-3-phenylpyrazoquinazoline*, $C_{16}H_9N_3Cl_2$, forms yellow needles, m. p. 160°; *7-amino-3-phenylpyrazoquinazoline*, $C_{16}H_{12}N_4$, forms white, silky needles, m. p. 215°; *7-ethoxy-3-phenylpyrazoquinazoline*, $C_{18}H_{15}ON_3$, crystallises in glistening, white needles, m. p. 136°; *3-phenyl-6-ethyldihydropyrazoquinazolone*, $C_{18}H_{15}ON_3$, forms glistening, white needles, m. p. 171°; the corresponding *6-phenyl* compound, $C_{22}H_{15}ON_3$, crystallises in pale yellow prisms, m. p. 211°; the corresponding *6-anilino*-compound, $C_{22}H_{16}ON_4$, forms glistening, yellow leaflets, m. p. 248°; the analogous *6-amino*-compound, $C_{16}H_{12}ON_4$, forms glistening, white leaflets, m. p. 232° (decomp.), the *benzylidene* derivative of which crystallises in slender, white needles, m. p. 185°; the *6-carbamide*, $C_{17}H_{13}O_2N_5$, forms felted, white needles, m. p. 325° (decomp.); the *6-oximino*-compound, $C_{16}H_{11}O_2N_3$, forms glistening, white needles, m. p. 247°; *1 : 3-diphenyl-5-pyrazolone-2'-carboxylic acid*, $\begin{matrix}CH_2{\cdot}CO\\ |\\ CPh{=}N\end{matrix}\!\!>\!N{\cdot}C_6H_4{\cdot}CO_2H$, crystallises in white, glistening leaflets, sinters at 189°, m. p. 197° (decomp.), and yields a *barium* salt ($3H_2O$), felted, white needles, *ethyl* ester,

$$C_{16}H_{11}O_2N_2{\cdot}OEt,$$

glistening, white needles, m. p. 133°, and *dichloro*-derivative,

$$\begin{matrix}CHCl{\cdot}CCl(OH)\\ |\\ CPh{=}\!\!=\!\!=\!\!=\!\!=N\end{matrix}\!\!>\!N{\cdot}C_6H_4{\cdot}CO_2H,$$

slender, white needles, m. p. 208° (decomp.); *1 : 3-diphenyl-4-benzylidene-5-pyrazolone-2'-carboxylic acid*, $C_{23}H_{16}O_3N_2$, forms glistening, white crystals, m. p. 241°; the corresponding *4-oximino*-compound, $C_{16}H_{11}O_4N_3$, crystallises in stout, scarlet needles, m. p. 213°; the

corresponding 4-*nitro*-compound, $C_{16}H_{11}O_5N_3$, forms glistening, yellow leaflets, m. p. 268° (decomp.); the 4-*benzeneazo*-compound, $C_{22}H_{16}O_3N_4$, forms compact, glistening, bright red crystals, m. p. 225°; the 4-*p*-*toueneazo*-compound, $C_{23}H_{18}O_3N_4$, crystallises in glistening, orange-red needles, m. p. 194°.

3-Phenylpyrazo*iso*coumarazone, when heated with phenol and aluminium chloride, yields the *substance*,

$$CPh\begin{matrix}\diagup N—N\cdot C_6H_4 \\ \diagdown CH:C---O\end{matrix}\diagup C(C_6H_4\cdot OH)_2,$$

an amorphous, yellowish-brown powder, m. p. 120°, solutions of which in aqueous alkalis are intensely red; an analogous *substance*,

$$C_{32}H_{30}ON_4,$$

is similarly obtained by condensation with dimethylaniline; it forms glistening, white leaflets, m. p. 216°; an intensely green *substance* is formed simultaneously.

3-Methylpyrazo*iso*coumarazone, when heated with resorcinol and zinc chloride, yields a *substance*, $C_{19}H_{14}O_5,2H_2O$, which crystallises in colourless, glistening needles, m. p. 186—187°, and dissolves in alkalis, forming solutions with an intense blue fluorescence; 3-phenylpyrazo*iso*coumarazone, when similarly treated, yields a *substance*, $C_{19}H_{12}O_4$, pale yellow, rectangular plates, m. p. 248°, solutions of which in alkali exhibit a yellowish-green fluorescence.

[With Christoph Käding.]—*3-Chloro-1-phenyl-5-methylpyrazole-2'-carboxylic acid*, $C_{11}H_9O_2N_2Cl$, is prepared by the oxidation of 3-chloro-1-*o*-tolyl-5-methylpyrazole with chromic acid; it crystallises with $1H_2O$ in white prisms, m. p. 79°; the anhydrous substance has m. p. 111°; the *barium* and *silver* salts were analysed; the *ethyl* ester,

$$C_{13}H_{13}O_2N_2Cl,$$

is a colourless oil, b. p. 325°. The acid when heated at 190° under a pressure of 16 mm. yields *5-methylbenzobis-3-pyrazolone*,

$$\begin{matrix}C_6H_4\cdot N\cdot CMe \\ CO—N--CO\end{matrix}\diagup CH,$$

crystallising in glistening, yellow leaflets, m. p. 265°, solutions of which in acetic acid, alcohol, and chloroform have a bluish-green or blue fluorescence; the 4-*bromo*-derivative, $C_{11}H_7O_2N_2Br$, forms yellow, matted needles, m. p. 233°, solutions of which in organic solvents exhibit a blue fluorescence. *1-Phenyl-5-methyl-3-pyrazolone-2'-carboxylic acid*, $C_{11}H_{10}O_3N_2$, is formed by dissolving 5-methylbenzobis-3-pyrazolone in aqueous alkali; it crystallises in white leaflets, m. p. 221°; the *ammonium* salt forms white prisms, m. p. 260°; the *ethyl* ester crystallises in white, slender prisms, m. p. 160°; the *amide*, $C_{11}H_{11}O_2N_3$, is formed by heating 5-methylbenzobis-3-pyrazolone with aqueous ammonia under pressure at 210°; it forms white crystals, m. p. 249°; the *anilide*, $C_{17}H_{15}O_2N_3$, white crystals, m. p. 161°, *phenylhydrazide*, $C_{17}H_{16}O_2N_4$, white leaflets, m. p. 218°, and *hydrazide*, $C_{11}H_{12}O_2N_4$, colourless crystals, m. p. 253°, are similarly prepared; the 4-*benzeneazo*-derivative, $C_{17}H_{14}O_3N_4$, forms yellowish-brown leaflets, m. p. 210°.

4-*Bromo*-1-*o*-*tolyl*-3-*methylpyrazole*, $C_{11}H_{11}N_2Br$, is prepared by brominating 1-*o*-tolyl-3-methylpyrazole; it is a colourless liquid with

a pleasant odour, b. p. 171°/25 mm., and when oxidised yields 4-*bromo*-1-*phenyl*-3-*methylpyrazole*-2′-*carboxylic acid*, $C_{11}H_9O_2N_2Br$, which crystallises in white prisms, m. p. 194°; the *silver* salt forms white needles; the *ethyl* ester is a colourless oil with a pleasant odour, b. p. 334°. W. H. G.

1-Phenyl-3-methyl-5-pyrazolone-3′- and 4′-carboxylic Acids. August Michaelis and Hans Horn (*Annalen*, 1910, 373, 213—218). —The 3′- and 4′-carboxylic acids of 1-phenyl-3-methyl-5-pyrazolone have the same chemical properties as the 2′-isomeride (compare this vol., i, 514), but the chloropyrazolecarboxylic acids derived from them, when heated, do not decompose with the elimination of hydrogen chloride.

Ethyl acetoacetate-4-*carboxyphenylhydrazone*,

$$CO_2Et\cdot CH_2\cdot CMe{:}N\cdot NH\cdot C_6H_4\cdot CO_2H,$$

is prepared from ethyl acetoacetate and 4-hydrazinobenzoic acid; it forms slightly yellow needles, and when heated at 150° yields 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4′-*carboxylic acid*, $C_{11}H_{10}O_3N_2$, pale yellow needles, m. p. 281°; the latter substance is converted (1) by benzaldehyde into the 4-*benzylidene* derivative,

$$C_{10}H_8O_3N_2\cdot C{:}CHPh,$$

dark red needles, m. p. 266°; (2) by sodium nitrite and acetic acid into the 4-*oximino*-derivative, $C_{10}H_8O_3N_2\cdot C{:}N\cdot OH$, yellow needles, decomposing at 253°; (3) by diazobenzene chloride into the 4-*benzeneazo*-derivative, $C_{10}H_8O_3N_2\cdot C{:}N_2Ph$, slender, yellow needles, m. p. 277°, and (4) by phosphoryl chloride into 5-chloro-1-phenyl-3-methylpyrazole-4′-carboxylic acid (compare Michaelis and Sudendorf, Abstr., 1900, i, 696).

The following compounds are similarly prepared: 1-*phenyl*-3-*methyl*-5-*pyrazolone*-3′-*carboxylic acid* forms slender, white needles, m. p. 217°; the *methyl* ester forms white crystals, m. p. 86°; the *ethyl* ester is a pale yellow oil, b. p. 241°/25 mm.; the 4-*benzylidene* derivative crystallises in red leaflets, m. p. 251°; the 4-*oximino*-derivative forms orange-red needles, m. p. 242°; the 4-*benzeneazo*-derivative forms orange-yellow leaflets, m. p. 245°; 5-*chloro*-1-*phenyl*-3-*methylpyrazole*-3′-*carboxylic acid* crystallises in small needles, m. p. 165°. 1-Phenyl-3-methyl-5-pyrazolone-3′-carboxylic acid (1 mol.) is converted by phosphorus pentachloride (2 mols.) under pressure at 136°, and subsequent treatment with water into 4 : 4-*dichloro*-1-*phenyl*-3-*methyl*-5-*pyrazolone*-3′-*carboxylic acid*,

$$C_{11}H_8O_3N_2Cl_2,$$

white needles, m. p. 116°. W. H. G.

Blue Reduction Product from Flavanthren. Julius Potschiwauscheg (*Ber.*, 1910, 43, 1748—1750).—Flavanthren, when reduced with alkaline sodium hyposulphite in an atmosphere of hydrogen, yields a mixture of products from which Scholl and Holdermann (Abstr., 1908, i, 696) by means of benzoyl chloride isolated *O*-benzoyldihydroflavanthren, an amorphous, reddish-brown powder.

Using *p*-bromobenzoyl chloride, a *mono*-p-*bromobenzoyldihydroflavanthren* is obtained, crystallising from nitrobenzene in yellow needles, which are not melted at 360°. This is insoluble in sodium

hydroxide; accordingly, the acyl residue is attached to oxygen. It dissolves in concentrated sulphuric acid with a green coloration, turning reddish-brown on heating. E. F. A.

Intramolecular Transformations. IV. Hydroxytriazoles and Diazoamides. Otto Dimroth [and, in part, Hans Aickelin, B. Brahn, Gustav Fester, and Elsa Merckle] (*Annalen*, 1910, **373**, 336—370. Compare Abstr., 1905, i, 98, 384; 1909, i, 267).—It has been shown previously that many 5-hydroxy-1 : 2 : 3-triazole derivatives are converted by fusion or by solution in organic solvents into neutral isomerides which have been regarded as triazolones, the change being one of enol-keto-desmotropy. Doubts of the correctness arose later when it was found that 5-aminotriazoles under the same conditions also underwent changes by detachment of the azo-group from one nitrogen atom and re-attachment to another; for example:

$$NR\!<\!\begin{matrix}C(NHR')\\ N{=}{=}N\end{matrix}\!>\!CH \longrightarrow NR'\!<\!\begin{matrix}C(NHR)\\ N{=}{=}N\end{matrix}\!>\!CH.$$

Assuming that the same change occurs in hydroxytriazoles, the neutral isomeride would be a substituted amino-derivative of a diazo-anhydride: $NR\!<\!\begin{matrix}C(OH)\\ N{=}N\end{matrix}\!>\!CH \longrightarrow O\!<\!\begin{matrix}C(NHR)\\ N{=}{=}N\end{matrix}\!>\!CH$. This explanation of the change of the hydroxytriazoles has been considered previously and rejected, because the properties of the neutral isomerides are not at all comparable with those of other diazo-anhydrides, the cyclic oxygen atom of which is very reactive (Wolff, Abstr., 1903, i, 203). Piloty and Neresheimer (Abstr., 1906, i, 146) have shown, however, that ethyl diazomalonate exhibits remarkable stability to acids and to iodine, and therefore formulate it as a diazo-anhydride, $\begin{matrix}C(CO_2Et){:}C(OEt)\\ N{=}{=}{=}{=}{=}{=}N\end{matrix}\!>\!O$. The oxygen atom is non-reactive, showing no tendency to be replaced by sulphur or amino-groups. The stability of ethyl diazomalonate is not remarkable when it is borne in mind how the reactivity of diazomethane is diminished by the introduction of one carbethoxy-group. Consequently, ethyl diazomalonate may be represented by the preceding formula or by the only alternative, $\begin{matrix}N\\ \|\\ N\end{matrix}\!>\!C(CO_2Et)_2$. The latter is accepted for the following reasons:

Ethyl diazomalonate is converted by cold ammonium hydroxide into ethyl diazomalonamate, $NH_2{\cdot}CO{\cdot}CN_2{\cdot}CO_2Et$, m. p. 143°, which is changed by sodium ethoxide into *ethyl* 5-*hydroxy*-1 : 2 : 3-*triazole*-4-*carboxylate*, $\begin{matrix}C(CO_2Et){:}C(OH)\\ N{=}{=}{=}{=}{=}{=}N\end{matrix}\!>\!NH$, m. p. 130°; the latter is reconverted into the former by fusion. If ethyl diazomalonate has the constitution ascribed to it by Piloty and Neresheimer, the substance produced by the action of ammonium hydroxide would be either $\begin{matrix}C(CO_2Et){:}C(NH_2)\\ N{=}{=}{=}{=}{=}{=}N\end{matrix}\!>\!O$ or $\begin{matrix}C(CO{\cdot}NH_2){:}C(OEt)\\ N{=}{=}{=}{=}{=}{=}{=}N\end{matrix}\!>\!O$, neither of which is satisfactory, since the substance does not contain a primary amino-group, and yields a hydroxytriazolecarboxylic ester (not an amide) by treatment with sodium ethoxide.

From the preceding, the author arrives at the conclusion that all the

neutral isomerides, obtained by the fusion or solution of 5-hydroxytriazoles and previously described as triazolones, possess a diazo-structure similar to that of ethyl diazomalonate, and are derivatives of diazomethane. This theory harmonises with the fact that the hydroxytriazoles are colourless, whilst their neutral isomerides are yellow, and explains such phenomena as the conversion of 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid into carbon dioxide and the corresponding hydroxytriazole by warm water, and the conversion of the neutral isomeride

$$\left[\text{new formula, } NHPh\cdot CO\cdot C(CO_2H)<\begin{matrix}N\\ ||\\ N\end{matrix}\right]$$

by the same means into nitrogen and glycolloanilide. The theory is supported by the two following facts. Aminomalonamide hydrochloride in aqueous solution, sodium nitrite, and a few drops of dilute sulphuric acid at 0° yields *diazomalonamide*, $\begin{matrix}N\\ ||\\ N\end{matrix}>C(CO\cdot NH_2)_2$, m. p. 175°, which forms yellow crystals, and is converted by sodium ethoxide into 5-*hydroxy*-1 : 2 : 3-*triazole*-4-*carboxylamide*,

$$\begin{matrix}C(CO\cdot NH_2):C(OH)\\ |\qquad\qquad\qquad|\\ N=\!=\!=\!=\!=\!=\!=\!=N\end{matrix}>NH,$$

m. p. 196°, which is colourless and reconvertible into diazomalonamide by prolonged boiling with alcohol. (The hydroxytriazole-amide is more conveniently prepared by acidifying the product obtained by the interaction of malonamide, phenylazoimide, and alcoholic sodium ethoxide.) The other fact is the reduction of the substance formerly described as methyl 1-phenyl-5-triazolone-4-carboxylate

$$\left[\text{now regarded as } NHPh\cdot CO\cdot C(CO_2Me)<\begin{matrix}N\\ ||\\ N\end{matrix}\right]$$

by alcoholic hydrogen sulphide to a *hydrazi*-compound,

$$NHPh\cdot CO\cdot C(CO_2Me)<\begin{matrix}NH\\ |\\ NH'\end{matrix},$$

m. p. 130—131°, which is colourless, does not decolorise iodine, yields hydrazine by treatment with boiling 10% hydrochloric acid, and is reconverted into the original substance by mercuric oxide; this behaviour is quite similar to that of the reduction product of ethyl diazomalonate.

The analogy between the desmotropic change of 5-hydroxytriazoles and of 5-aminotriazoles, which apparently disappears in the new explanation of the former change, reappears with the assumption of the formation of a fugitive intermediate compound in the case of the aminotriazoles; thus, $\begin{matrix}C(CO_2R):C(NH_2)\\ |\qquad\qquad\qquad|\\ N=\!=\!=\!=\!=\!=\!=\!=N\end{matrix}>NPh \longrightarrow$

$$NPh:C(NH_2)\cdot C(CO_2R)<\begin{matrix}N\\ ||\\ N\end{matrix} \longrightarrow \begin{matrix}C(CO_2R):C(NHPh)\\ |\qquad\qquad\qquad|\\ N=\!=\!=\!=\!=\!=\!=\!=N\end{matrix}>NH.$$

It appears, therefore, that there is an intimate connexion between hydroxytriazoles of the type $\begin{matrix}CR':C(OH)\\ |\qquad\qquad|\\ N=\!=\!=\!=\!=\!=\!=N\end{matrix}>NR$ and diazoamides, $NHR\cdot CO\cdot CR'<\begin{matrix}N\\ ||\\ N\end{matrix}$. The latter are converted quantitatively and universally into salts of the former by alkaline reagents. The

converse change, hydroxytriazole $\longrightarrow$ diazoamide, by fusion or solution in organic solvents is not general, and depends on the nature of R and R'. 5-Hydroxytriazole, 5-hydroxy-1-phenyltriazole, 5-hydroxy-1-phenyl-4-methyltriazole, and 5-hydroxy-1 : 4-diphenyltriazole cannot be changed into the isomeric diazoamides. The presence of CO_2R or of $CO{\cdot}NH_2$ in position 4 facilitates the change into the diazo-compound, which is also favoured by the presence of phenyl and especially of negatively-substituted phenyl groups in position 1; thus methyl 5-hydroxy-1-*o*-*p*-dinitrophenyl-1 : 2 : 3-triazole-4-carboxylate has so great a tendency to change that it is only stable in the form of its salts. Also, when *p*-nitrophenylazoimide and methyl sodiomalonate react in methyl alcohol, and the product is acidified and recrystallised from acetic acid, the yellow *diazo*-compound,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}C(CO_2Me)\!<\!\overset{N}{\underset{N}{\|}},$$

m. p. 175°, is obtained, the expected colourless hydroxytriazole, $\overset{N}{\underset{N}{\|}}\!\!>\!C(CO_2Me){\cdot}C(OH)\!>\!N{\cdot}C_6H_4{\cdot}NO_2$, only being produced by treating the yellow isomeride with sodium methoxide.

The stabilising influence of a positive radicle in position 1 is shown in the case of *methyl 5-hydroxy-1-benzyl-1 : 2 : 3-triazole-4-carboxylate*, m. p. 119°, which is obtained from benzylazoimide, methyl malonate, and methyl alcoholic sodium methoxide, and subsequent acidification of the product; it is colourless, and can be recrystallised from organic solvents without change, although by fusion it is converted into the yellow *diazo*-compound, $CH_2Ph{\cdot}NH{\cdot}CO{\cdot}C(CO_2Me)\!<\!\overset{N}{\underset{N}{\|}}$, m. p. 45°.

Methods of measuring the velocities of the opposed reactions, hydroxytriazole $\rightleftharpoons$ diazo-compound, are described, and the values are tabulated and discussed. C. S.

Urazoles. XVI. Salts of Tautomeric Compounds. Reactions of Urazole Salts with Alkyl Halides. Roger F. Brunel and Salomon F. Acree (*Amer. Chem. J.*, 1910, **43**, 505—553. Compare Abstr., 1908, i, 919).—An account is given of a study of the alkylation of potassium phenylurazole by various alkyl iodides. The chief product of these reactions is the *N*-ester of the urazole, and, in most cases, evidence was obtained of the presence of some *O*-ester. In the case of the *iso*butyl and *iso*amyl compounds, only traces of *O*-derivatives could be detected, whilst in other cases the amount appeared to be 10—20% of the total product.

The application of the results of these experiments to the general question of tautomerism is discussed. It is shown that the assumption of different structures for the potassium and silver salts of a tautomeric compound does not afford an explanation of the urazole reactions, since both salts yield a mixture of *O*- and *N*-esters. The theory that when a salt gives two isomeric derivatives on alkylation, one is an intermediate product in the formation of the other, does not hold in the present case, because neither derivative undergoes rearrangement into the other, and the ratio of the two products is almost the same at all

stages of the reaction. The addition theory is not valid in the case of the urazoles, since in many reactions the velocity decreases on the addition of electrolytes, whereas, according to this theory, it should increase. The results can all be explained, however, by assuming the existence of two tautomeric salts in instantaneous equilibrium.

The following compounds have been obtained: 1-*phenyl*-2-*ethylurazole*, m. p. 119°; 1-*phenyl*-2-n-*propylurazole*, m. p. 128°; 1-*phenyl*-2-n-*butylurazole*, m. p. 130°; 1-*phenyl*-2-iso*propylurazole*, m. p. 161·5°; 1-*phenyl*-2-iso*butylurazole*, m. p. 152·5°; 1-*phenyl*-2-iso*amylurazole*, m. p. m. p. 97—98°. The *silver* salts of all these compounds, except the last, have been prepared. 1-*Phenyl*-4-n-*propylurazole* has m. p. 120°; 1-*phenyl*-4-n-*butylurazole*, m. p. 149—150°, and 1-*phenyl*-4-*methyl*-2-*ethylurazole*, m. p. 52—53°.

In carrying out the quantitative investigation of the reaction of the alkyl halides with urazole salts, it was necessary to maintain sealed tubes at a particular temperature for a considerable time. For this purpose a special constant-temperature water-bath was devised, which is regulated automatically and can be kept at any temperature up to 100° with a variation of not more than 0·1—0·2°. This apparatus is described. E. G.

Degradation of 7 : 9-Dimethyluric Acid. Heinrich Biltz and Paul Krebs (*Ber.*, 1910, 43, 1589—1600).—When 7 : 9-dimethyluric acid 4 : 5-diglycol (Fischer's oxy-7 : 9-dimethyluric acid : compare this vol., i, 526) is heated with water or with glacial acetic acid on the water-bath for several hours, it is transformed into an isomeride, which is represented as 5-*hydroxy*-1 : 3-*dimethylhydantoin*-5-*carbureide* or 5-*hydroxy*-1 : 3-*dimethylhydantoylcarbamide*,

$$NH_2\cdot CO\cdot NH\cdot CO\cdot C(OH)<\begin{matrix}NMe\cdot CO\\ CO-\!-NMe\end{matrix},$$

which crystallises from a mixture of ether and alcohol. It has m. p. 208° (decomp.), and when decomposed with sodium hydroxide solution at the ordinary temperature is transformed into the corresponding acid, which immediately loses water, yielding the lactone,

$$\begin{matrix}{}^{7}NH\cdot{}^{6}CO\\ CO-\!-O\end{matrix}>{}^{5}C<\begin{matrix}{}^{1}NMe\cdot{}^{2}CO\\ {}^{4}CO-\!-{}^{3}NMe\end{matrix},$$

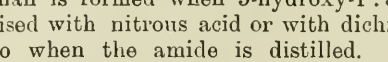
which is closely related to certain degradation products of caffeine, and is therefore termed 1 : 3-*dimethylcaffolide*. It crystallises from chloroform in flat, monoclinic rhombohedra, m. p. 163—164° (decomp.). A quantitative yield of the same compound can be obtained by treating an alcoholic solution of hydroxydimethylhydantoylcarbamide with hydrogen chloride.

When boiled with water, the dimethylcaffolide takes up a molecule of water and loses carbon dioxide, yielding 1 : 3-*dimethylhydantoylamide*, $NH_2\cdot CO\cdot C(OH)<\begin{matrix}NMe\cdot CO\\ CO-\!-NMe\end{matrix}$, which crystallises in large, mono- or tri-clinic prisms, m. p. 180—182° (decomp.). The *ethyl ether*,

$$NH_2\cdot CO\cdot C(OEt)<\begin{matrix}NMe\cdot CO\\ CO-\!-NMe\end{matrix},$$

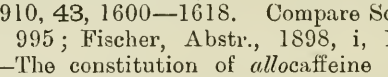
obtained by saturating the alcoholic solution with hydrogen chloride, crystallises in six-sided prisms, m. p. 189—190°, and the *diacetyl* derivative, $C_{10}H_{13}O_6N_3$, crystallises in flat, rectangular prisms, m. p. 172—173°.

Cholesterophan is formed when 5-hydroxy-1 : 3-dimethylhydantoylamide is oxidised with nitrous acid or with dichromate and sulphuric acid, and also when the amide is distilled. Mesoxalic acid and dimethylcarbamide are formed when the amide is boiled with barium hydroxide solution. Hydrogen peroxide and ammonia react with the amide, yielding cholesterophan and formic acid. When heated at 210°, the amide loses carbon dioxide and yields a product, m. p. 330° (decomp.), which is regarded as 5-*hydroxy*-1 : 3-*dimethylhydantoin*-5-*carboxylic acid lactamide*,



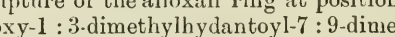
J. J. S.

Degradation of Tetramethyluric Acid. *allo*Caffeine. Heinrich Biltz (*Ber.*, 1910, **43**, 1600—1618. Compare Schmidt and Schilling, Abstr., 1885, 995; Fischer, Abstr., 1898, i, 180; Torrey, Abstr., 1899, i, 86).—The constitution of *allo*caffeine has been established by its synthesis from 1 : 3-dimethylcaffolide (compare preceding abstract) by the methylation of the *silver* salt, $C_7H_6O_5N_3Ag$, and by means of methyl iodide and silver oxide. *allo*Caffeine is therefore 1 : 3 : 7-*trimethylcaffolide*,



The degradation of tetramethyluric acid to *allo*caffeine probably proceeds in the following stages: (1) Oxidation to the corresponding glycol; (2) rupture of the alloxan ring at position 3 : 4, and formation of 5-hydroxy-1 : 3-dimethylhydantoyl-7 : 9-dimethylcarbamide; (3) hydrolysis to methylamine and the hydroxy acid; (4) elimination of water and formation of the lactone.

Attempts have been made to prepare tetramethyluric acid glycol by the condensation of dimethylalloxan with dimethylcarbamide, but the reaction proceeds further, and methylamine and *allo*caffeine are the only products obtained. This method is the most convenient for the preparation of *allo*caffeine, especially when the condensation is carried out in the presence of dilute hydrochloric acid (1 : 2) at the ordinary temperature, as under these conditions a 95% yield of *allo*caffeine is obtained at the end of two days. *allo*Caffeine can also be obtained by the condensation of methylalloxan with dimethylcarbamide, and by the methylation of 5-hydroxy-1 : 3-dimethylhydantoylcarbamide (preceding abstract) with methyl sulphate.

*allo*Caffuric acid, obtained by boiling an aqueous solution of *allo*caffeine (Torrey, *loc. cit.*), has m. p. 168·5—169·5° after it has been once fused. This method of formation is analogous to the conversion of 1 : 3-dimethylcaffolide into 5-hydroxy-1 : 3-dimethylhydantoylamide (preceding abstract). *allo*Caffuric acid is therefore 5-*hydroxy*-1 : 3-*dimethylhydantoylmethylamide*,  , and its reactions are in complete harmony with this constitution. When

distilled, it yields cholesterophan and methylformamide, and when hydrolysed with barium hydroxide yields methylamine, mesoxalic acid, and dimethylcarbamide.

5-*Acetyl*allo*caffuric acid*, $C_9H_{13}O_5N_3$, crystallises in well-developed twinned prisms, m. p. 194·5—195·5°. The *ethyl ether*, 5-*ethoxy*-1 : 3-*dimethylhydantoylmethylamide*, $NHMe\cdot CO\cdot C(OEt)<^{NMe\cdot CO}_{CO—NMe}$, obtained by saturating an alcoholic solution of the hydroxy-compound with hydrogen chloride at 0°, crystallises in well-developed, monoclinic prisms, m. p. 112—113°. The corresponding *methyl ether*, $C_8H_{13}O_4N_3$, has m. p. 121—122°.

1 : 3-*Dimethylhydantoylmethylamide* (*deoxy*allo*caffuric acid*), $NHMe\cdot CO\cdot CH<^{NMe\cdot CO}_{CO—NMe}$, obtained by reducing *allo*caffuric acid with hydriodic acid (D = 1·96), crystallises from alcohol in flat prisms, m. p. 180°, after sintering at 170°, and can be oxidised by chlorine water to *allo*caffuric acid.

*allo*Caffeine reacts with a cold 33% alcoholic methylamine solution, yielding *allo*caffuric acid and dimethylcarbamide. The reaction probably consists in the addition of methylamine to the *allo*caffeine, yielding 5-hydroxytetramethylhydantoylcarbamide, which at once reacts with methylamine, forming *allo*caffuric acid and dimethylcarbamide. Ethylamine and ammonia react in a similar manner.

Schmidt and Schilling's caffeinemethylhydroxide (*loc. cit.*) is to be represented by the formula : $CO<^{NMe\cdot CO\cdot C\cdot NMe}_{NMe—C\cdot NMe(OH)}>CH$.

J. J. S.

*apo*Caffeine and the Degradation of 1 : 3 : 7-Trimethyluric Acid and of Caffeine. Heinrich Biltz and Paul Krebs (*Ber.*, 1910, 43, 1618—1632. Compare Fischer, Abstr., 1882, 217, 628; 1897, i, 267—268).—*apo*Caffeine is 1 : 7-*dimethylcaffolide*, $^{NMe\cdot CO}_{CO—O}>C<^{NMe\cdot CO}_{CO—NH}$, as its *silver* salt, $C_7H_6O_5N_3Ag$, yields *allo*caffeine when treated with silver oxide and methyl iodide. Similarly, caffuric acid is 5-hydroxy-1-methylhydantoylmethylamide, as it yields *allo*caffuric acid when methylated.

The best method of obtaining *apo*caffeine is the oxidation of caffeine with potassium chlorate and concentrated hydrochloric acid (compare Maly and Andreasch, Abstr., 1882, 629). When dilute hydrochloric acid is used, and excess of acid is avoided, an isomeride, *isoapo*caffeine, is also formed; the proportions are *apo*caffeine four-fifths, and the *iso*-compound one-fifth. The same *iso*-compound is also formed by the action of potassium chlorate and hydrochloric acid on trimethyluric acid or on chlorocaffeine. It crystallises in four-sided pyramids or in lancet-shaped plates, decomposes at 176—177°, and when methylated yields *allo*caffeine. *apo*Caffeine and *isoapo*caffeine can be synthesised from methylcarbamide and dimethylalloxan in hydrochloric acid solution, and this appears to be the most convenient

method for the preparation of *apo*caffeine; a trimethyluric acid glycol could not be isolated.

The *ethyl ether* of caffuric acid, 5-*ethoxy*-1-*methylhydantoylmethyl-amide*, $NHMe\cdot CO\cdot C(OEt)<^{NMe\cdot CO}_{CO---NH}$, crystallises in compact prisms, m. p. 220—221°. J. J. S.

Carbon–Nitrogen Linkings. Heinrich Biltz (*Ber.*, 1910, 43, 1632—1636).—It is pointed out that the affinities existing between nitrogen and carbon are analogous to the affinities which take part in salt formation.

The compounds formed increase in stability as the basic nature of the nitrogen and the acidic nature of the carbon are increased and vice versa. This accounts for the stability of the glycols formed from 7 and 9 alkylated uric acids. Such compounds when decomposed suffer rupture in the alloxan ring.

Noticeable is the fact that the introduction of methyl groups into the alloxan ring facilitates decomposition to such an extent that it has not been found possible to isolate the glycols of tri- and tetramethyluric acids.

Similar relationships are met with in the glycols derived from diphenylglyoxalones. Various other examples are cited. J. J. S.

Dihydrazines. III. Julius von Braun (*Ber.*, 1910, 43, 1495—1505. Compare Abstr., 1908, i, 700, 737).—4 : 4′-Bismethylhydrazinodiphenylmethane (diphenylmethanedimethyldihydrazine) reacts readily with diketones at the ordinary temperature, but only one carbonyl group takes part in the reaction.

Acetonylacetone and 2 : 9-undecandione (Abstr., 1907, i, 893) yield thick, oily condensation products. Acetylacetone yields a *product*, $CH_2(C_6H_4\cdot NMe\cdot N{:}CMe\cdot CH_2Ac)_2$, m. p. 144°, and benzoylacetone, a *product*, $CH_2(C_6H_4\cdot NMe\cdot N{:}CPh\cdot CH_2Ac)_2$, which crystallises in yellow plates, m. p. 147°. Diacetyl yields a product which melts at about 100°.

Contrary to Kohlrausch's statement (Abstr., 1890, 24), it is found that *as*-phenylmethylhydrazine also reacts readily with diketones in acetic acid solution. *Acetylacetonephenylmethylhydrazone*,

$$CH_2Ac\cdot CMe{:}N\cdot NMePh,$$

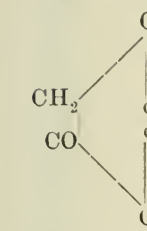
forms long, prismatic crystals, m. p. 98°, and b. p. 165°/12 mm.; the benzoylacetonephenylmethylhydrazone has m. p. 80°, not 103—104°.

Cyclic ketones containing the group $-CH_2\cdot CO\cdot CH_2-$, and in addition several side-chains, react with the dihydrazine and a little sulphuric acid in the same manner as the ketones described previously (Abstr., 1908, i, 737), but not quite so readily; in each case ammonia is evolved, and an amorphous carbazole condensation product sparingly soluble in alcohol is obtained.

Ethyl 1-methyl*cyclo*hexan-5-one-2-carboxylate yields a product, which on hydrolysis gives an *acid* decomposing at about 200°. The *acid*, obtained by hydrolysing the condensation product from ethyl 1 . 3-dimethyl*cyclo*hexan-5-one-2-carboxylate, has m. p. 171°. Dihydro-*iso*phorone yields a *product*, which sinters at 167° and melts at 180°;

ethyl dihydro*iso*phoronecarboxylate, a *product*, m. p. 102°; and ethyl 1-phenyl*cyclo*hexan-3-one-5-acetate, a *product*, which melts at 175° after sintering at 155°.

Carvone, thujone, diosphenol, and dimethyldi*cyclo*nonanolone (Rabe, Abstr., 1908, i, 554) do not react with the dihydrazine. The non-reactivity of the last-mentioned compound indicates that its constitution is probably that of a di*cyclo*octane derivative (annexed formula).



Arabinose, rhamnose, galactose, and mannose react readily with the dihydrazine. Ketoses, dextrose, xylose, glucosamine, lactose, maltose, raffinose, and sucrose do not react. This difference is undoubtedly due to spatial relationships of the hydroxyl groups. The hydrazones formed from arabinose, rhamnose, galactose, and *d*-mannose are obtained in theoretical amount, and can be readily isolated from aqueous alcoholic or dilute acetic acid solutions, as they are sparingly soluble. The products melt respectively at 180° (decomp.), 163°, 185°, 179°. Mixtures of mannose and dextrose and of arabinose and xylose can be separated easily by means of the different behaviour of the sugars towards the dihydrazine.

Diphenylmethanediethyldihydrazine, $CH_2(C_6H_4\cdot NEt\cdot NH_2)_2$, is an oil; it yields a sparingly soluble *sulphate* and a *semicarbazide*,

$$CH_2(C_6H_4\cdot NEt\cdot NH\cdot CO\cdot NH_2)_2,$$

obtained by the action of potassium cyanate, m. p. 215°.

The diethyldihydrazine yields hydrazones with aromatic aldehydes, which can be obtained in a crystalline form from pyridine. Benzaldehyde yields a *product*, $CH_2(C_6H_4\cdot NEt\cdot N{:}CHPh)_2$, in the form of colourless, glistening plates, m. p. 161°; anisaldehyde, a *product*, $CH_2(C_6H_4\cdot NEt\cdot N{:}CH\cdot C_6H_4\cdot OMe)_2$, m. p. 142°; glyoxal yields a solid *hydrazone*, $CH_2<\begin{matrix}C_6H_4\cdot NEt\cdot N{:}CH\\ C_6H_4\cdot NEt\cdot N{:}CH\end{matrix}$, but most aliphatic aldehydes yield oily hydrazones. The sugars react somewhat more slowly with the diethyl compound. Mannose yields a *hydrazone*,

$$CH_2(C_6H_4\cdot NEt\cdot N{:}C_6H_{12}O_5)_2,$$

m. p. 183°. J. J. S.

Behaviour of Certain Ureides and Purine Substances towards Sodium Benzoate Solutions. Giovanni Pellini and Mario Amadori (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 480—487).—The authors have measured the variations produced in the freezing points of water and of solutions of sodium benzoate of a number of different, fixed concentrations by the addition of increasing quantities of certain ureides and purine derivatives (compare this vol., i, 416). The results show that carbamide and urethane behave normally in water and in sodium benzoate solutions. Diethylbarbituric acid ("veronal") gives normal depressions of the freezing point of water, and even with concentrated solutions of sodium benzoate there is neither an appreciable increase of solubility nor sufficient variation of the freezing point to indicate the formation of a compound between the veronal and sodium benzoate. Alloxan behaves normally in water, but forms a

compound with sodium benzoate; allantoin exhibits similar behaviour. The slight solubility of uric acid in water does not appear to be increased in presence of sodium benzoate, whilst the solubility of theobromine is apparently augmented to some extent. Theophylline increases in solubility in presence of sodium benzoate.

No clear relation exists between the dissociation constants of these different compounds and their tendencies to form complexes with sodium benzoate, although caffeine has the smallest dissociation constant and the greatest capacity for complex formation.

T. H. P.

Uric Acid Glycols. Heinrich Biltz and Paul Krebs (*Ber.*, 1910, **43**, 1511—1519).—A comparison of the formulæ of 7 : 9-dimethyluric acid and 1 : 3-dimethyl-4 : 5-diphenylglyoxalone and their oxidation (Abstr., 1908, i, 218) points to the conclusion that Fischer's oxy-7 : 9-dimethyluric acid (Abstr., 1884, 1309) is the glycol:

$$CO\begin{<}NH\cdot CO\cdot C(OH)\cdot NMe\\ NH\text{——}C(OH)\cdot NMe\end{>}CO.$$

This view is shown to be correct, as Fischer's compound can be synthesised by heating together alloxan and dimethylcarbamide, either alone or in acetic acid or concentrated aqueous solution. These methods are much more convenient that Fischer's for the preparation of the glycol. When its solution in glacial acetic acid is heated for a long time, an isomeride is formed. The crystals of the glycol are triclinic, and show cleavage along the base; the angle $b : a = 96°$, $c : a = 98°$, and $a : b = 99°$.

Methylcarbamide and alloxan yield a *methyluric acid glycol*, $C_6H_8O_5N_4$, which crystallises in flat prisms or plates, m. p. 208—209° (decomp.), and it is not so soluble as the dimethyl derivative.

7 : 9-*Diethyluric acid glycol*, $C_9H_{14}O_5N_4$, crystallises in monoclinic prisms, begins to melt at 105°, and becomes quite clear at 120°.

Ethyluric acid glycol, $C_7H_{10}O_5N_4$, crystallises in glistening plates, which decompose at 198—200°. J. J. S.

Hexanitrohydrazobenzene and Salts of Trinitrodiphenylamine. Arthur Hantzsch and Joseph Lister (*Ber.*, 1910, **43**, 1685—1688).—When a solution of hexanitrohydrazobenzene in methyl alcohol or acetonitrile is evaporated in a desiccator, a residue is obtained of the yellow, real hexanitrohydrazobenzene, together with a red mass which probably consists of a compound of the *aci*-nitro-form and the solvent, since by warming or by treatment with acids the red mass loses weight and changes into yellow hexanitrohydrazobenzene. This view is supported by spectrometric evidence. Yellow solutions of hexanitrohydrazobenzene show only general absorption, whilst red solutions yield absorption spectra very similar to those of the alkali salts of the hexanitro-compound. C. S.

The Refractive Indices of Solutions of Certain Proteins. T. Brailsford Robertson (*J. Biol. Chem.*, 1910, **7**, 359—364).—If n is the refractive index of the solution, n_1 of the solvent (distilled water, 1·3333 at 18°), c the percentage concentration of the protein, and a a constant equal to the change in the refractive index produced by

dissolving 1 gram in 100 c.c., then $n - n_1 = ac$. The values of a for ovomucoid, ovo-vitellin, and caseinogen respectively are 0·00160, 0·00130, and 0 00152. W. D. H.

Adsorption Compounds of Certain Proteins with Inorganic Haloid Salts Soluble in Alcohol. Friedrich Simon (*Zeitsch. physiol. Chem.*, 1910, 66, 70—87).—Certain haloid salts (calcium chloride, bromide and iodide, strontium chloride, and lithium chloride) which are soluble in alcohol, when mixed with proteins and protein digestion products in aqueous solutions are precipitated with the proteins in definite quantities on the addition of alcohol. The removal of the salts by washing or by re-solution and precipitation is very difficult and never complete. The precipitates form brown powders on drying, which dissolve easily in warm water; the solutions exhibit the typical reactions of the anions and cations of the salts used; these are present in the same proportions as in the salts. W. D. H.

Calorimetric Investigations of the Precipitation of Proteins by Salts of Heavy Metals. Tullio Gayda (*Biochem. Zeitsch.*, 1910, 25, 341—358).—The author determined the heat of reaction when salts of heavy metals in varying strengths of solution are added to protein solutions, and by analysis, the composition of the precipitate formed. If a precipitate is formed in the case of copper salts, there is a fall of temperature. This is the algebraical sum of the heat of solution and the heat of precipitation, which latter factor is negative. This latter is itself the algebraical sum of the heat of precipitation of protein (0·4025 cal. for 1 gram protein, which number is independent of the protein concentration in solution) and the heat of adsorption of copper sulphate by the protein ($-20·1621$ cal. for 1 gram of copper sulphate). In greater concentrations, when no precipitate is formed, the heat of reaction is the algebraical sum of the heat of dilution of the copper sulphate solution and a residual heat which is negative, and which indicates that even when no precipitate is formed, a complex of protein and copper sulphate is formed. When a precipitate is formed by mercuric salts, the heat of reaction is positive. The conditions here are somewhat more complex than in the case of copper salts, as the heat of adsorption of mercury salts by the protein complex is a function of two variables; namely, the quantity of protein precipitated and the mercury salt carried down with this precipitate. The heat of adsorption of 1 gram of mercuric chloride is a parabolic function of the quantity of protein precipitated. S. B. S.

A Protein Substance in the Pancreatic Juice. Elkan Wechsler (*Zeitsch. physiol. Chem.*, 1910, 66, 284—286).—The protein in pancreatic juice is not a nucleo-protein, nor a gluco-protein. It gives Millon's and the biuret reactions. It contains 13·2% nitrogen. It yields in parts % of the total nitrogen: ammonia, 0·3, humin I, 10·9; humin II, 5·4; histidine, 4·1; arginine, 15·7; lysine, 1·3; and mono-amino-acids, 56·9. In parts % of the total protein, the following figures are given: arginine, 6·44; histidine, 1·99; lysine, 0·89; ammonia, 0·05. It is thus poor in lysine, and very poor in ammonia. W. D. H.

Rate of Solution of Casein in Solutions of the Hydroxides of the Alkalis and of the Alkaline Earths. T. Brailsford Robertson (*J. Physical. Chem.*, 1910, 14, 377—392. Compare also Abstr., 1908, i, 930).—When casein is stirred at an approximately constant rate in solutions of the hydroxides of the alkalis or of the alkaline earths, the amount dissolved is given by the equation $x = kt^m$, where x is the number of grams of casein dissolved, t is the time which has elapsed since the casein was introduced into the solvent, and k and m are constants depending on the concentration and nature of the hydroxide solution and on the total mass of casein in the mixture.

Within the errors of experiment, the rapidity of solution is not affected by the temperature for temperatures ranging between room temperature and 30°.

Equally concentrated solutions of the hydroxides of potassium, sodium, lithium, and ammonium dissolve casein at approximately the same rate. Solutions of the hydroxides of the alkaline earths dissolve casein much more slowly, strontium hydroxide dissolving it the most, and barium hydroxide the least, rapidly.

The amount of casein dissolved by a solution of potassium hydroxide in a given time is directly proportional to the concentration of the hydroxide.

The velocity of solution of the casein increases with the mass of casein present in the mixture. The rate of increase of the velocity of solution with increasing mass of the casein is at first rather large, but it becomes much less as the mass of the casein is still further increased.

In the light of the above results, it is suggested that the factor which determines the rate of solution of casein in the alkaline solutions mentioned is the velocity with which the casein particles are penetrated and moistened by the solvent. T. S. P.

Partial Hydrolysis of Casein. Zdenko H. Skraup and E. Krause (*Monatsh.*, 1910, 31, 149—163. Compare Skraup and Hummelberger, Abstr., 1908, i, 711 ; Skraup and Woeber, *ibid.*, 1909, i, 446 ; Skraup and Lampl, *ibid.*, i, 537).—The products obtained by shaking casein with 60% sulphuric acid have been examined. It has been found possible to isolate a product very sparingly soluble in water, and resembling casein in many respects ; this is termed albumose I. Among the products precipitated on the addition of ammonium sulphate, the one obtained when the solution is one-fourth saturated is formed in appreciable amount and is termed albumose II. A product which is not precipitated by ammonium sulphate is termed peptone. All three products were hydrolysed with concentrated hydrochloric acid, and the amounts of tyrosine and glutamic acid determined. The peptone did not yield any tyrosine, but the two albumoses gave somewhat larger yields than the casein itself. Albumose II gave far less glutamic acid than the original casein, whereas the peptone gave much the same amount, and albumose I somewhat more. The following colour-reactions of the three products were also examined : Millon's, glyoxylic acid, biuret, β-naphthol, and thymol. J. J. S.

Cleavage Products obtained by the Partial Hydrolysis of Proteins. Emil Abderhalden and Akikazu Suwa (*Zeitsch. physiol. Chem.*, 1910, 66, 13—18).—From Canton silk, glycyl-*d*-alanine anhydride and glycyl-*l*-tyrosine anhydride were obtained. From Neuchang silk and Indian tussore, *d*-alanine anhydride and glycyl-*d*-alanine anhydride were obtained. By the partial hydrolysis of Italian grège and Canton silk, alanine anhydride was not obtained.

W. D. H.

Blood Colouring Matter. William Küster (*Zeitsch. physiol. Chem.*, 1910, 66, 165—249. Compare this vol., i, 210).—Dehydrochloridehæmin undergoes changes on keeping which hinder the simple addition of hydrogen chloride and reformation of hæmin. Hæmin crystals are obtained from dehydrochloridehæmin by the action of hydrochloric acid, but hæmatin prepared by the action of alkalis on hæmin does not behave similarly. Hæmin dissolves both in aniline and in *p*-toluidine, owing to salt formation, but not in *o*-toluidine; this is ascribed to steric hindrance.

In the preparation of hæmatoporphyrin any oxidation in acid solution is to be avoided, and therefore sulphuric or hydrochloric acid should not be used. The iron eliminated is tervalent. Hæmin is more resistant to acids than hæmatin or dehydrochloridehæmin. Acetic acid acts but weakly on hæmatin, even at high temperatures.

Hæmin and hæmatin are insoluble in acid carbonates and diacid phosphates; with normal carbonates, acid carbonates are formed. The disodium salt of hæmatin gives up a molecule of sodium hydroxide on prolonged dialysis. Solutions of the alkali salts of hæmatin polymerise on keeping.

Precipitates obtained with metallic salts have not the exact composition: $C_{34}H_{30}O_4MN_4FeOH$. In the iron and silver salts, the metal seems to be fixed in a complex salt, and in such salts the attachment of the iron in hæmatin is rendered looser.

Typical hæmin is not obtained by Eppinger's method, and only in admixture with another substance by Sievert's method. The longer hæmatin remains in alkaline solution, the more difficult it is to prepare typical hæmin from it. The solution of hæmatin obtained by decomposing the barium compound with sulphuric acid and alcohol, when treated with hydrochloric acid at 50—72° gives a product soluble in alkali, but at 80° an insoluble product partly esterified is produced.

In hæmin the group $>$FeCl, in hæmatin $>$FeOH, replace the imide hydrogen of the pyrrole ring; the acid properties of the two substances are due to the presence of two carboxyl groups. In passing into dehydrochloridehæmin, hydrogen chloride is eliminated between one of these and the group $>$FeCl. In the reduction of hæmatin to hæmochromogen, ferric are reduced to ferrous compounds. The addition of carbon dioxide to hæmochromogen, or of oxygen, carbon dioxide or nitrous oxide to hæmoglobin, takes place at the iron. E. F. A.

The Non-Existence of "Protagon" in the Brain. Otto Rosenheim and M. Christine Tebb (*Biochem. Zeitsch.*, 1910, 25, 151—160).—The authors maintain, in opposition to Wilson and

Cramer, that the so-called "protagon" is not a simple substance. A product can be obtained which on repeated recrystallisation from small quantities of alcohol does not vary very appreciably in composition; if, however, larger quantities of alcohol or other solvents be employed for recrystallisation, the "protagon" can be separated into fractions of varying composition, especially as regards the phosphorus content (from 0·07 to 3·13%). The authors give some details as to the composition of fractions obtained in various recrystallisations.

S. B. S.

Some Colloid-Chemical Aspects of Digestion with Ultramicroscopic Observations. Jerome Alexander (*J. Amer. Chem. Soc.*, 1910, **32**, 680—687).—After drawing attention to the fact that the catalytic action of enzymes probably depends on the preliminary formation of a compound of the enzyme with the substrate, it is pointed out that this product is most likely a colloidal absorption compound, and it is suggested that enzymes produce their effects by virtue of their specific surface actions and the motion of their particles. This view has been confirmed by observations with the ultramicroscope. When starch grains were treated with a solution of diastase, ultramicrons in rapid motion were seen to accumulate about the starch grains, which after a time showed an indented outline. The bright appearance of the field indicated the presence of numerous finer particles, whilst some particles of an intermediate size were visible. A solution of egg-albumin which had been heated nearly to boiling was opalescent, and, when viewed with the ultramicroscope, presented a field full of bright and rapidly moving ultramicrons. On adding a pepsin solution containing 15% of alcohol, immediate coagulation took place. On addition of dilute hydrochloric acid, the coagulated masses became disintegrated, and ultramicrons again appeared as before. The albumin particles gradually decreased in size, and eventually disappeared.

Reference is made to the action of reversible colloids in protecting irreversible or unstable colloids from coagulation, and consequently enabling colloidal sols to pass through membranes otherwise impermeable to them. This principle of colloidal protection has been demonstrated with the aid of the ultramicroscope. The casein particles in milk are seen to be in active motion, but if dilute acid is added, they immediately coagulate. If, however, a little gelatin or gum arabic is introduced before acidifying, coagulation is prevented, and the casein particles continue in motion. Gelatin exerts a greater protective action than gum, and is able to protect casein from coagulation by rennin.

E. G.

The Fatal Temperature for Plant Tyrosinases. Gabriel Bertrand and M. Rosenblatt (*Compt. rend.*, 1910, **150**, 1142—1145; *Bull. Soc. chim.*, 1910, [iv], **7**, 557—561. Compare Abstr., 1907, i, 811).—The view that more than one specific tyrosinase exists gains support from the fact that some enzymes of this type are more resistant to heat than others. The temperature at which the enzyme ceases to be capable of developing a coloration with tyrosine

has been determined for a number of preparations of different origin. Thus the fatal temperature for the tyrosinase from *Amanita rubescens* is 60—65°; from *Russula queletti*, *R. rubra*, and *R. delica*, 65—70°; from lentils and potatoes, 80—85°, and for that from the root of beetroot, 90—95°. The temperature for any particular enzyme is only slightly influenced by the nature of the solvent and the mode of preparation; furthermore, in mixtures containing more than one, each diastase behaves as if the others were absent. W. O. W.

Action of Hypophosphorous Acid on Dinaphthapyranol. Dinaphthapyrylphosphinous Acid. Robert Fosse (*Bull. Soc. chim.*, 1910, [iv], 7, 357—359).—Dinaphthapyrylphosphinous acid, the formation of which has been described already (this vol., i, 292), forms small, white crystals, which develop a superficial reddish-violet coloration, and in alcoholic solution reduces silver nitrate. The *sodium* salt forms brilliant silvery crystals from water, which become opaque on drying, and gradually develop a reddish-violet tint. The *barium* salt separates in crystals from hot water. T. A. H.

Preparation and Properties of *p*-Iodophenylarsinic Acid and Certain of its Derivatives. I. Efisio Mameli and Aldo Patta (*Gazzetta*, 1910, 40, i, 128—137).—Part of the work here described has been already published (Abstr., 1909, i, 543).

p-*Iodophenylarsenious oxide*, $C_6H_4I\cdot AsO$, obtained, together with hydriodic acid, by the action of water or an alkali carbonate or hydroxide on *p*-iodophenylarsenious iodide (*loc. cit.*), forms a straw-coloured powder, m. p. 245—250°.

p-*Di-iodoarsenobenzene*, $C_6H_4I\cdot As{:}As\cdot C_6H_4I$, prepared by reducing *p*-iodophenylarsinic acid by means of phosphorus acid, is a yellow substance, m. p. 145—150°, insoluble in all organic solvents.

T. H. P.

Preparation of Homologues of *p*-Aminophenylarsinic Acid. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 219210).—In the well-known preparation of magenta by heating *o*- and *m*-toluidines with arsenic acid, the latter acts simply as an oxidising agent; the methods are now described by which it is induced to become a substituting agent.

o-Toluidine (90 parts) is heated in a distilling apparatus, and finely-powdered arsenic acid (24 parts) slowly stirred in, the temperature being maintained with continual stirring at 165—168° during about an hour, when water and *o*-toluidine distil over; the internal temperature is then raised to 185—190° during an equal period, the apparatus cooled, and the contents treated with water, rendered alkaline with calcium or barium hydroxide, and any residual toluidine removed with steam. The liquid is saturated with sodium chloride, and, after twenty-four hours, filtered, and the liquid just acidified with hydrochloric acid, when a resinous by-product separates, and, after a further twenty hours, the pure 4-*amino*-3-*tolylarsinic acid* is precipitated in needles, m. p. 194—195°. The *sodium* salt is crystalline, and can be separated from its aqueous solution by addition of alcohol.

4-*Amino*-2-*tolylarsinic acid*, m. p. 180°, is similarly prepared from *m*-toluidine.

4-*Amino*-2 : 5-*xylylarsinic acid*, from *p*-xylidine, crystallises with $1H_2O$, and when anhydrous has m. p. 215°. These compounds are colourless, and are readily soluble in hot, sparingly in cold, water; they yield crystalline salts, and diazotise readily with nitrous acid; their therapeutic germicidal action is analogous to that of *p*-aminophenylarsinic acid. F. M. G. M.

Action of Organo-magnesium Compounds on Boron Trichloride, Sulphur Chloride, and on the Chloride and Esters of Sulphurous Acid. Wilhelm Strecker (*Ber.*, 1910, **43**, 1131—1136).—When magnesium phenyl bromide reacts with boron trichloride, only one chlorine atom is replaced, so that the final product is always phenylboric acid (compare Khotinsky and Melamed, Abstr., 1909, i, 864). This acid cannot be titrated in the ordinary way, but it is more dissociated than boric acid, the molecular conductivity at 25° being 0·133. On the assumption that the conductivity at infinite dilution is the same as that of benzoic acid, this gives a degree of dissociation of 0·00027 at 25°, while that of boric acid is 0·00012 (Walker and Cormack, Trans., 1900, **77**, 5).

Magnesium phenyl bromide reacts with sulphur chloride (S_2Cl_2), yielding phenyl disulphide; diphenyl is also formed.

As a result of the action of magnesium phenyl bromide and magnesium benzyl bromide on thionyl chloride, the corresponding sulphoxides are formed, in addition to diphenyl and benzyl sulphide. With *s*-diethyl sulphite the same sulphoxides are obtained. *as*-Diethyl sulphite and magnesium phenyl bromide yield phenyl ethyl sulphone.

The action of magnesium ethyl iodide and magnesium phenyl bromide on benzene solutions of nitrogen chloride (Hentschel, Abstr., 1897, ii, 447) was tried without result. R. V. S.

Action of Thionyl Chloride on Organo-magnesium Compounds. Victor Grignard and L. Zorn (*Compt. rend.*, 1910, **150**, 1177—1179. Compare Strecker, preceding abstract).—Thionyl chloride resembles carbonyl chloride in its action on organo-magnesium compounds (Abstr., 1903, i, 455). When 1 mol. of the chloride is employed with 2 mols. of an aromatic magnesium compound, a sulphinone is produced, whilst if a greater proportion (3 mols.) of the magnesium derivative is taken, a sulphonium complex, of the type $SR_3 \cdot OMgX$, is formed. When X is an aliphatic radicle, this undergoes decomposition in two directions: (1) $SR_3 \cdot OMgX = SR_2 + MgX \cdot OR$; (2) $SR_2(OMgX) \cdot C_nH_{2n+1} = SR_2 + MgX \cdot OH + C_nH_{2n}$.

From the magnesium derivative of bromoquinol dimethyl ether, a small quantity of bis-2 : 5-dimethylphenylsulphinone, $[C_6H_3(OMe)_2]SO$, was obtained, in the form of small crystals, m. p. 124—125°.

W. O. W.

Organic Chemistry.

Purification and the Physical Constants of Some Organic Liquids. Jean Timmermans (*Bull. Soc. chim. Belg.*, 1910, 24, 244—268).—The author gives a general discussion of the precautions which are necessary in the purification of an organic liquid by fractional distillation. Twenty-five different compounds have been investigated, the criteria of purity being the boiling point and the density. In some cases the freezing point and the critical solution temperature in an inert solvent were also used as criteria.

The following table gives a summary of the results. In each case the ± refers to variations in the last decimal place given.

Substance.	B. p. /760 mm.	*dt*/*dp* for 10 mm.	$D^{0°}_{4°}$
*iso*Pentane	27·95°±1	0·37°	0·63942±3
Ethyl bromide	38·40 ±1	0·36	1·50138±2
Ethylene dichloride	83·70 ±1	—	1·2838±2
Chloroform	61·20 ±1	0·35	1·52635±2
Carbon tetrachloride	76·75 ±1	0·44	1·63255±2
Carbon disulphide	46·25 ±1	0·42	1·29272±2
Acetonitrile	81·60 ±1	0·30	0·80350±1
Ethylamine	16·55 ±1	0·28	0·70570±10
Methyl alcohol	64·70 ±1	0·30	0·81017±3
Ethyl ether	34·60 ±1	0·36	0·73627±3
Acetone	56·10 ±1	0·30	0·81249±3
Methyl ethyl ketone	79·60 ±2	0·38	0·82551±1
Methylal	42·30 ±2	0·40	0·88548±2
*iso*Butyric acid	154·35 ±2	0·32	0·96819±2
Methyl formate	31·75 ±2	0·34	1·00340±3
Ethyl acetate	77·15 ±1	0·41	0·90476±2
Ethyl propionate	99·10 ±1	0·40	0·91245±2
Toluene	110·70 ±1	0·42	0·88448±2
Chlorobenzene	132·00 ±1	0·49	1·12795±1
Bromobenzene	156·15 ±1	0·53	1·52193±1
Benzonitrile	191·30 ±1	0·54	1·02279±3
Nitrobenzene	210·85 ±1	0·48	1·22290±4
Aniline	184·40 ±1	0·51	1·03895±2
Anisole	153·80 ±2	0·48	1·01237±2
Pyridine	115·50 ±1	0·44	1·00302±2

T. S. P.

The First Synthesis of Ethyl Alcohol. Raphael Meldola (*J. Soc. Chem. Ind.*, 1910, 29, 737—740).—An historical paper in which the author maintains his thesis that Henry Hennel was the first to synthesise ethyl alcohol (compare Berthelot, Abstr., 1899, i, 471; Fritsche, 1902, i, 657). T. S. P.

Molecular Compounds of Alcohol and Water. T. Fawssett (*Pharm. J.*, 1910, [iv], 30, 754—757).—This paper is largely the mathematical exposition of a theory proposed to explain the contraction occurring when ethyl alcohol and water are mixed. According to

the theory advanced, when ethyl alcohol and water combine the first compound formed is invariably $(C_2H_6O)_{18},H_2O$, which subsequently combines with successive molecules of water, forming an indefinite number of compounds. Further, that the formation of each molecular compound or "system" causes a definite contraction of the total volume, and that the contraction is proportional to the weight of the water in the equation: $(C_2H_5\cdot OH)_9,H_2O + H_2O = (C_2H_5\cdot OH)_9,2H_2O$. From the latter it is deduced that the contraction $\overset{(n)}{r}$ resulting on the formation of the compound $(C_2H_6O)_{18},nH_2O$ from the compound $(C_2H_6O)_{18},(n-1)H_2O$ is equal to $\{5\cdot136n/(23+n) - 5\cdot136(n-1)/[23+(n-1)]\}$ of the volume of water added. The contractions $\left(\overset{(n)}{r}\right)$ produced by nine successive additions of 5/18 gram-molecules of water to 5 gram-molecules of ethyl alcohol were measured at 15·5° in an apparatus described. The observed contractions diminish from 0·221 for the first addition to 0·113 for the ninth, the calculated figures varying from 0·214 to 0·119, whilst the difference only amounts to 0·01 in three instances. E. H.

αα-Dialkyl-*β*-keto-alcohols. Edmond E. Blaise and I. Herman (*Ann. Chim. Phys.*, 1910, [viii], 20, 173—194).—Recapitulates work recorded already in Abstr., 1907, i, 749; 1908, i, 78, 248, 319, 596; 1909, i, 85, and continues the work dealt with in Abstr., 1909, i, 632. The following data are new. Kling and Viard's statement (Abstr., 1904, i, 545) that tertiary alcohols are dehydrated at the boiling point of naphthalene could not be verified in the cases of trimethylcarbinol or *α*-hydroxydi*iso*propyl ketone, $CHMe_2\cdot CO\cdot CMe_2\cdot OH$. The primary alcohol, *ethyl hydroxy*-sec.-*butyl ketone*, $OH\cdot CH_2\cdot CHEt\cdot COEt$, b. p. 102·5°/13 mm., is also stable under these conditions.

α-Hydroxydi*iso*propyl ketone, the formation of which has been described already (Abstr., 1908, i, 319), furnishes a *p-nitrophenylhydrazone*, m. p. 127·5°, crystallising in yellow needles. Attempts to synthesise this hydroxy-ketone from ethyl *α*-hydroxy-*iso*valerate by the action of magnesium methyl iodide resulted in the production of *βδ-dimethylpentane-βγ-diol*, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot OH$, m. p. 59°, which crystallises in colourless needles, and yields a *monoacetyl* derivative, $CHMe_2\cdot CH(OAc)\cdot CMe_2\cdot OH$, b. p. 88—89°/11 mm., and a *phenylurethane*, m. p. 127°. This glycol on oxidation with chromic acid gives a mixture of ketones, but no *α*-hydroxydi*iso*propyl ketone. On dehydration with sulphuric acid, the glycol yields di*iso*propyl ketone (Abstr., 1904, i, 219).

The following details are given of the compounds prepared in the course of the synthesis of ethyl tiglyl ketone (Abstr., 1908, i, 596): *β*-hydroxy-*α*-methylbutyric acid furnishes a *phenylurethane*, m. p. 128°, crystallising in slender needles. The acetyl derivative of the acid yields an *ethyl* ester, b. p. 97·5°/15 mm., a *p-toluidide*, m. p. 129°, slender needles, an *α naphthylamide*, m. p. 126°, and an *acid chloride*, b. p. 84°/13 mm. The last-mentioned substance condenses with zinc ethyl iodide to give *β-acetoxy-α-methylpropyl ethyl ketone*,

$$OAc\cdot CHMe\cdot CHMe\cdot COEt,$$

b. p. 97—97·5°/14 mm., and this on hydrolysis in the cold furnishes a

mixture of the corresponding *hydroxy-ketone*, b. p. 89—90°/14 mm., and ethyl tiglyl ketone, b. p. 50·5°/13 mm.; the latter absorbs hydrogen bromide, but the bromo-compound formed is unstable, and could not be isolated. T. A. H.

Hydrogenation of Acetylenic Compounds. Robert Lespieau (*Compt. rend.*, 1910, **150**, 1761—1762).—Reduction of unsaturated glycols, such as the compound $OH\cdot CH_2\cdot C{:}C\cdot C{:}C\cdot CH_2\cdot OH$ or

$$OH\cdot CH_2\cdot C{:}C\cdot C{:}C\cdot CH_2\cdot OH,$$

by means of platinum black and hydrogen in alcoholic or ethereal solution results in the production of a good yield of the corresponding saturated glycols. Small quantities of hexane and hexanol are also formed in the case of the latter compound. The yield is considerably diminished if the dimethyl ethers of the glycols are employed, owing to the formation of saturated hydrocarbons and of dimethyl ether. W. O. W.

Hydroxydiacetyl. Otto Diels and Milan Farkaš (*Ber.*, 1910, **43**, 1957—1962).—It has not been found possible to obtain a monobromo-derivative of diacetyl, the only product formed by direct bromination being the dibromo-derivative (compare Fittig, Keller, and Daimler, Abstr., 1889, 491). Diacetylmonoxime yields a monobromo-derivative when dissolved in methyl alcohol and treated with bromine at 0°, and this reacts with a methyl alcoholic solution of potassium acetate, yielding the corresponding acetyl derivative, which, when hydrolysed with barium hydroxide solution, yields the oxime of hydroxydiacetyl; but, so far, it has not been found possible to obtain hydroxydiacetyl itself.

Modifications of Diels and Jost's method (Abstr., 1902, i, 744) for the preparation of diacetylmonoxime are recommended. Its *bromo*-derivative, $CH_2Br\cdot CO\cdot CMe{:}N\cdot OH$, crystallises from benzene, has m. p. 83—84°, and attacks the mucous membrane. The *acetate*,

$$OAc\cdot CH_2\cdot CO\cdot CMe{:}N\cdot OH,$$

forms snow-white crystals, m. p. 93·5—94°. It yields a *phenylhydrazone*, $OAc\cdot CH_2\cdot C(:N_2HPh)\cdot CMe{:}N\cdot OH$, which forms sulphur-yellow, dichroic crystals, m. p. 132—133° (corr.).

Hydroxydiacetylmonoxime, $OH\cdot CH_2\cdot CO\cdot CMe{:}N\cdot OH$, crystallises from water in large, brilliant prisms, m. p. 118·5—119·5° (corr., decomp.), and yields a *phenylhydrazone*, $OH\cdot CH_2\cdot C(:N_2HPh)\cdot CMe{:}N\cdot OH$, which crystallises from alcohol in long, pale yellow, refractive needles, m. p. 197·5° (corr.).

Hydroxydiacetylosazone, $OH\cdot CH_2\cdot C(:N_2HPh)\cdot CMe{:}N_2HPh$, obtained by the action of an excess of phenylhydrazine on a dilute acetic acid solution of the monoxime, crystallises in golden-yellow plates, m. p. 189° (corr., decomp.) J. J. S.

Attempts to Transform Nitrous Vapours into the Corresponding Calcium Salts by the Use of Ethyl Nitrite and Nitrate. Eugène Tassilly and J. Leroide (*Bull. Soc. chim.*, 1910, [iv], **7**, 622—628).—Nitrous vapours are absorbed fairly completely by ethyl alcohol with the formation of ethyl nitrite and nitrate, but the resulting solution on treatment with lime does not furnish good

yields of the corresponding calcium salts, so that this method cannot be used for the conversion of waste nitrous fumes into calcium salts of industrial value.

Nitric oxide, obtained by the action of nitric acid on copper, was mixed with air, previously purified by passing over (1) pumice stone mixed with potassium hydroxide, and (2) pumice stone saturated with sulphuric acid, to form a mixture containing 1 to 2% of nitrous fumes, and this was drawn through alcohol kept at $-20°$, then through glass wool at $-35°$ to $-40°$, to eliminate alcohol, etc., from the issuing gas, and finally through a tube containing diphenylamine in sulphuric acid. The last tube served as a test for nitrous vapours in the issuing gas, and its subsequent examination showed that the proportion of nitrous vapours which escaped absorption was less than 1×10^{-5} of that dissolved by the alcohol. The alcoholic solution at first contains ethyl nitrite and ethyl nitrate, but, when kept, part of the nitrate is hydrolysed, and the nitric acid formed reacts with the excess of alcohol to form acetaldehyde. Experiments on the hydrolysis of ethyl nitrite and nitrate in alcohol with potassium hydroxide showed that good yields of the potassium salts could be obtained, but with lime under similar conditions the hydrolysis of ethyl nitrite is negligible at atmospheric temperature or 100°, but amounts to 23·1% at 140°, and with ethyl nitrate amounts to 29·0 and 55·0% at 140° and 150° respectively. Potassium is not displaced from potassium nitrite or nitrate by boiling with lime in presence of alcohol. T. A. H.

Ethyl Metaphosphate and its Use in Organic Chemistry. Kurt Langheld (*Ber.*, 1910, 43, 1857—1860).—*Ethyl metaphosphate*, $C_2H_5PO_3$, can be prepared by the action of ethyl iodide on silver metaphosphate, but is more readily obtained by the action of phosphoric oxide on anhydrous ethyl ether, $OEt_2 + P_2O_5 = 2EtPO_3$. It forms a thick syrup, and may be purified by solution in chloroform and precipitation with ether. It is readily hydrolysed by alkalis, and when boiled with ethyl alcohol gives a mixture of di- and tri-ethyl phosphates.

The metaphosphate when boiled with chloroform and dextrose yields two organic phosphorus compounds, from which crystalline barium salts have been obtained.

Leucine reacts with a chloroform solution of ethyl metaphosphate, yielding the compound: $PO(OEt)(OH)\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CHMe_2$.

The metaphosphate is a good condensing agent, as it eliminates water or ammonia very readily from mixtures of organic compounds.

J. J. S.

Formation and Decomposition of Thiols; Synthesis of Dialkyl Sulphides. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1910, 150, 1569—1572. Compare this vol., i, 456).—Attempts have been made to improve the yield of thiols from secondary alcohols when these are submitted to the catalytic process already described. Substitution of the oxides of zirconium, uranium, tungsten, chromium, molybdenum, or aluminium for the thorium oxide previously employed resulted in diminished yields in the case of *iso*amyl alcohol and of phenol.

Metallic sulphides have a catalytic effect on thiols precisely similar to that exercised by alumina on alcohols, and if cadmium sulphide is used, the reaction affords a convenient method for the preparation of dialkyl sulphides. When passed over this substance at 320—330°, ethyl hydrogen sulphide is converted into diethyl sulphide, whilst at 380° decomposition into ethylene and hydrogen sulphide occurs. With secondary thiols, the yield of dialkyl sulphide is smaller, and the tendency to undergo decomposition more marked. The reaction is represented as (1) $CdS + 2C_nH_{2n+1}\cdot HS = Cd(S\cdot C_nH_{2n+1})_2 + H_2S$; (2) $Cd(S\cdot C_nH_{2n+1})_2 = CdS + (C_nH_{2n+1})_2S$. W. O. W.

Basic Ferric Acetate Contained in the Former Official Solution of Ferric Acetate. Rudolf F. Weinland (*Arch. Pharm.*, 1910, 248, 337—345).—The addition of sodium platinichloride in slight excess to the former official solution of ferric acetate of the D.A.-B. III causes a precipitation of the orange-red platinichloride, $\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]_2^1PtCl_6,5H_2O$, described previously (Abstr., 1909, i, 872). The basic acetate in the official solution, therefore, is the monoacetate, $\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]OAc$. C. S.

Colloidal Properties of Soluble Soaps. Filippo Botazzi and C. Victoroff (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 659—665).—The soap employed consisted chiefly of sodium oleate with smaller quantities of palmitate, stearate, etc. When a concentrated solution of it is dialysed, the volume of liquid in the dialyser at first increases, and the clear solution becomes opalescent and finally milky. This is due to the gradual hydrolysis of the soap; the alkali formed diffuses out, and fatty acids and acid soaps are precipitated. At the end of the dialysis, the liquid forms three layers, two, at the surface and at the bottom respectively, consisting of the acids and the acid soaps, and a third, intermediate, milky layer, which is a microgranular suspension of these substances in a very dilute solution of soap. A small quantity of soap is also lost by diffusion during the dialysis. When examined electrically, both the soap and the granules in the dialysed liquid are found to move towards the anode. On adding water or small quantities of *N*/10-sodium hydroxide to the concentrated soap solution, a gradual decrease of the viscosity occurs. When *N*/10-sodium hydroxide is added to the turbid, filtered liquid after dialysis, the viscosity at first increases, then decreases to its former value. If water is now added, the viscosity again slowly rises, owing to the decrease in concentration of the alkali present. The addition of an excess of sodium hydroxide causes precipitation of the soap. The concentrated soap solution has a very low surface tension, whilst that of the liquid after dialysis is not much less than that of distilled water. The variation of surface tension caused by addition of sodium hydroxide is similar to the changes produced in the viscosity, but in the reverse direction; when the viscosity increases the surface tension diminishes, and vice versa. R. V. S.

Hydrolytic Decomposition of Aqueous Alcoholic Solutions of Alkali Soaps. David Holde [with H. Döscher and G. Meyerheim] (*Zeitsch. Elektrochem.*, 1910, **16**, 436—442).—When a solution of a soap in aqueous alcohol is made exactly neutral to phenolphthalein and then shaken with a solvent such as benzene, the solution becomes red and the benzene contains some of the fatty acid of the soap, showing that the neutral solution is hydrolysed to some extent. The hydrolysis diminishes as the concentration of the alcohol increases, and practically disappears in 80% alcohol. The bearing of this on the accuracy of titrations of fatty acids is discussed.

The partition of oleic acid between "benzine" and aqueous alcohol is also studied. With 40% alcohol, 99·8% of the acid passes into the "benzine." T. E.

Carbohydrate Esters of Higher Fatty Acids. W. R. Bloor (*J. Biol. Chem.*, 1910, **7**, 427—430. Compare Neuberg and Pollak, this vol., i, 157).—Mannitol has been condensed with stearic acid under the influence of concentrated sulphuric acid at 65—75°, the mixture being then cooled and ether added (Grün's method).

A certain amount of ethyl stearate is formed as a by-product, and this complicates the purification of the condensation product. After repeated precipitation from its methyl alcoholic solution, *mannide distearate*, $C_6H_8O_2(C_{18}H_{35}O_2)_2$, was obtained as a colourless, semi-translucent, amorphous mass, which crystallised from ether in microscopic needles, m. p. 51°. It has $[\alpha]_D^{20} + 63{\cdot}9°$, and is readily hydrolysed by alcoholic sodium hydroxide solution. J. J. S.

Ester Condensation: Ethyl Oxalate and Propionitrile. Wilhelm Wislicenus and Wilhelm Silberstein (*Ber.*, 1910, **43**, 1825—1836).—The ordinary Claisen condensation (ethyl acetoacetate formation) is termed *ester condensation*. Three factors are of importance: the ester, the methylene derivative, and the condensing agent. According to Claisen the ester first forms an additive compound with the sodium alkyloxide. The most reactive ester is ethyl oxalate, then follow ethyl formate, nitrite, acetate, benzoate, and nitrate. The most reactive methylene compounds are benzyl cyanide, ketones, ethyl acetate, fluorene, etc. Freund and Speyer (Abstr., 1902, i, 584) have found that sodamide is a more effective condensing agent than sodium ethoxide. The authors recommend the use of potassium ethoxide in cases where sodium ethoxide gives but poor yields or produces no condensation at all; thus ethyl oxalate and propionitrile do not condense in the presence of sodium ethoxide (Fleischhauer, Abstr., 1893, 397), but with potassium ethoxide in the presence of anhydrous ether give an 83% yield of ethyl *β*-cyano-*α*-ketobutyrate after the mixture has been kept for three days at the ordinary temperature. The *potassium* compound, $C_7H_8O_3NK$, crystallises from alcohol in slender, colourless prisms, m. p. 162—163°, when freshly prepared. The salt is stable, is not hygroscopic, and is not decomposed by carbonic or acetic acids. The *sodium* salt is less soluble, and the *silver* and *copper* salts form precipitates. *Ethyl β-cyano-α-ketobutyrate*, $CN{\cdot}CHMe{\cdot}CO{\cdot}CO_2Et$, crystallises from benzene

in large, yellow prisms, m. p. 66—67° and b. p. 123°/17 mm. It dissolves to an appreciable extent in water, yielding acid solutions. When freshly liberated from its potassium salt, the ester gives a pale coloration with alcoholic ferric chloride, but the coloration increases with the time. This points to the liberation of the ketonic form and its gradual passage into the enolic form: $CN\cdot CMe{:}C(OH)\cdot CO_2Et$.

The *ammonium* salt, $C_7H_{12}O_3N_2$, forms colourless crystals, m. p. 113—114°.

A 20% yield of *β-cyano-α-ketobutyric acid* (propionitrileoxalic acid), $CN\cdot CHMe\cdot CO\cdot CO_2H$, can be obtained by dissolving the ester in ether and a little alcohol, and passing in hydrogen chloride and shaking with a little water. It forms yellow needles, m. p. 207—208°.

When hydrolysed with 20% aqueous potassium hydroxide, the ester yields propionic and oxalic acids (acid hydrolysis), but when hydrolysed with 25% sulphuric acid the product is propionylformic acid, m. p. 151—152° (compare Wislicenus and Arnold, Abstr., 1888, 361) (ketonic hydrolysis).

When warmed with dilute potassium hydroxide at 40°, or when treated with alkaline hydrogen peroxide at 40° (Radziszewski's method), the ester yields *oxalpropionamide*, $NH_2\cdot CO\cdot CHMe\cdot CO\cdot CO_2H$; this is best isolated as its *phenylhydrazone*, $C_{11}H_{13}O_3N_3$, which crystallises in glistening, colourless plates, m. p. 171—172°.

An 87% yield of the *anil*, $CN\cdot CHMe\cdot C(CO_2Et){:}NPh$, is obtained by gently warming the ester with aniline; it crystallises from ether in yellow, flat plates, m. p. 115—116°. If the mixture is heated for some time, aniline oxalate is formed.

The ester yields an *oxime*, $CN\cdot CHMe\cdot C(:N\cdot OH)\cdot CO_2Et$, in the form of colourless prisms, m. p. 104—105°, and a *phenylhydrazone*,

$$CN\cdot CHMe\cdot C(CO_2Et){:}N_2HPh,$$

in the form of yellow plates, m. p. 124—126°. The phenylhydrazone, when heated gradually to 200°, undergoes molecular rearrangement, and yields an isomeric *compound*, m. p. 109—111°, which is probably a pyrazole derivative, $NPh<\begin{matrix}C(NH_2){:}CMe\\ |\\ N=\!=\!=C\cdot CO_2Et\end{matrix}$.

The ester reacts with an alcoholic solution of hydrazine hydrate, yielding the *hydrazone* of *β-cyano-α-ketobutyrohydrazide*,

$$CN\cdot CHMe\cdot C(:N_2H_2)\cdot CO\cdot NH\cdot NH_2,$$

which crystallises in colourless prisms, m. p. 190—192°.

When brominated in chloroform solution, the ester yields *ethyl β-bromo-β-carboxylamido-α-ketobutyrate*, $NH_2\cdot CO\cdot CMeBr\cdot CO\cdot CO_2Et$, which crystallises in colourless, slender prisms, m. p. 134—135°.

The potassium derivative of ethyl β-cyano-α-ketobutyrate, when boiled for several days with alcoholic ethyl iodide, yields *ethyl β-cyano-β-methyl-β-ethylpyruvate* (*ethyl β-cyano-α-keto-β-methylvalerate*),

$$CN\cdot CMeEt\cdot CO\cdot CO_2Et,$$

as a colourless oil, b. p. 130°/24 mm., which yields α-methylbutyric acid when hydrolysed with potassium hydroxide solution and methylethylpyruvic acid when hydrolysed with dilute sulphuric acid. The phenylhydrazone of the pyruvic acid has m. p. 132—133° (compare Locquin, Abstr., 1906, i, 929).

A cold solution of diazobenzene chloride reacts with the potassium salt of ethyl β-cyano-α-ketobutyrate, yielding the phenylhydrazone of acetyl cyanide (Favrel, *Bull. Soc. chim.*, 1902, [iii], 27, 194). The potassium salt reacts with *p*-nitrobenzoyl chloride, yielding the *p-nitrobenzoyl* derivative, $CN\cdot CMe:C(CO_2Et)\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, as colourless plates, m. p. 83—84°, which are readily hydrolysed.

J. J. S.

Cork. III. Max von Schmidt (*Monatsh.*, 1910, 31, 347—356. Compare Abstr., 1904, i, 501).—It has been shown previously that the extract of cork meal in chloroform or other indifferent solvent contains cerin and about 10% of glycerides, and that about 30% of fatty acids, but no glycerides, are obtained by heating the residue with alcoholic potassium hydroxide; hence the fatty acids in cork are not present as glycerides and are insoluble. Since they cannot be combined with the cerin, which would be found in the alcoholic solution if such were the case, it follows that they must be present as anhydrides or as insoluble polymerides. This conclusion is justified by experiments on phellonic acid—the acid obtained from cork which has been examined most thoroughly. When this acid is heated for fifty-four hours at the b. p. of xylene, or for six hours with fuming hydrochloric acid in a water-bath, it is converted into an *anhydride*, m. p. 102°, which, however, is soluble in chloroform and in benzene; hence this anhydride is probably present in cork, its non-extraction by chloroform being due to the fact that it is embedded in the insoluble constituents of the cork. If this is so, the crude fatty acids obtained from cork should yield an insoluble product by heating. Experiment proves this, for at 140° the crude acids are converted into a brown, elastic, transparent mass, which is insoluble in indifferent solvents and is impermeable by gases. In fact, by heating a mixture of the crude acids and an equal weight of sawdust at 140°, a product is obtained which closely resembles natural cork in colour, elasticity, and workability and other properties, and differs from it only by the absence of its characteristic structure.

The substance to which the conversion of these fatty acids into an insoluble form is chiefly due is suberic acid, which is converted by heating, without loss of water and in the absence of air, into an insoluble, elastic mass, probably of a polymeride.

Cork, therefore, consists of an insoluble mixture of anhydrides and polymerides of solid and liquid fatty acids, together with the glycerides of these acids. Young cork most probably contains only glycerides, which in course of time, under the influence of air, light, and probably also of enzymes, are hydrolysed, the glycerol being oxidised to carbon dioxide and water; the fatty acids partly polymerising and partly forming anhydrides.

C. S.

Complex Iridium Derivatives. Iridiodichlorodinitro-oxalates. Maurice Vèzes and Alexis Duffour (*Bull. Soc. chim.*, 1910, [iv], 7, 507—512. Compare *Proc. verb. Soc. Sci. Bordeaux*, July 18, 1901).—*Tripotassium iridiodichlorodinitro-oxalate*,

$$K_3IrCl_2(NO_2)_2C_2O_4,2H_2O,$$

obtained by boiling potassium iridiodichloro-oxalate (Abstr., 1909, i, 762) in concentrated aqueous solution with potassium nitrite, crystallises in orthorhombic, orange-yellow needles ($a:b:c=0{\cdot}59101:1:0{\cdot}81461$). It is stable at ordinary temperatures, loses $2H_2O$ and becomer yellow at 100—120°, evolves nitrous fumes at 250°, and decomposes completely at 275°, leaving a black residue having the shape of the original crystals and consisting of iridium, potassium chloride, and potassium nitrite. No deflagration occurs. The salt does not give reactions for chloride, nitrite, or oxalate.

The *silver* salt obtained by interaction between solutions of the potassium salt and of silver nitrate, the latter in excess, crystallises in anhydrous, microscopic, birefringent, bright yellow lamellæ of rhombic form and having an acute angle 65°. The crystals give extinction with crossed nicols in a direction oblique to the diagonal. The salt is stable even above 100°, but begins to turn brown at 120°, and decomposes completely at 260°, but does not deflagrate. It undergoes double decomposition with hydrochloric acid or chlorides.

T. A. H.

Complex Derivatives of Iridium. Iridiodichlorodinitro-oxalic Acid and Salts. Alexis Duffour (*Bull. Soc. chim.*, 1910, [iv], 7, 512—516).—The acid could not be isolated, but was obtained in solution by adding the equivalent amount of hydrochloric acid to the silver salt (see preceding abstract). This solution on evaporation even under reduced pressure evolved nitrous fumes, leaving eventually a black residue containing iridium. Salts of this acid can be prepared by (1) double decomposition with the potassium salt; (2) action of chlorides on the silver salt, or (3) by neutralisation of the aqueous solution of the acid. The salts have generally the properties recorded already for the potassium and silver salts (*loc. cit.*). They are very soluble in water, with the exception of the silver and thallous salts. Salts of the following metals were prepared: *Rubidium*, *cæsium*, *thallium*, *ammonium*, *lithium*, and *sodium*. The last three crystallise with $2H_2O$. The hydrated ammonium salt is unstable and loses its water at atmospheric temperatures when kept over sulphuric acid, and some anhydrous crystals isomorphous with those of the rubidium salt separate with the hydrated salt in preparing the latter. The ammonium salt also differs from the others in deflagrating when heated.

T. A. H.

By-Products Obtained During the Replacement of the Alkyl Groups in Ethyl Malonate. Telemachos Komnenos (*Monatsh.*, 1910, 31, 421—438).—It has been shown (this vol., i, 361) that methyl ethanetetracarboxylate is the chief product obtained by the addition of iodine to the reaction product of ethyl malonate and sodium methoxide. The oily product of the reaction has now been examined. The portion which solidifies after a few days' keeping is probably *methyl acetone-aaγ-tricarboxylate*, $CH(CO_2Me)_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Me$, m. p. 105—108° (*phenylhydrazone*, m. p. 125°), although its properties are not analogous to those of the ethyl ester described by Willstätter. The alcoholic mother liquor of the preceding ester contains a small quantity of

another *substance*, $C_9H_{12}O_7$, m. p. 120°, not identical with, but possibly the enolic form of, the preceding ester, and also a *substance*, $C_{12}H_{16}O_9$, m. p. 75° (*phenylhydrazone*, m. p. 108—110°), which is probably *methyl γ-hydroxyhexan-βδ-dione-aaε-tricarboxylate*, formed by the elimination of 2 mols. of methyl alcohol and 1 mol. of carbon dioxide from 2 mols. of methyl malonate and 1 mol. of methyl tartronate (which is produced by the action of iodine and water on methyl sodiomalonate).

The remaining oily portion of the original by-product is found to consist chiefly of an *ester*, $C_9H_{12}O_7$, m. p. 97° (*phenylhydrazone*, m. p. 117—120°), which is isomeric, but not identical, with the ester first mentioned; it also contains an *ester*, $C_{14}H_{18}O_{11}$, m. p. 85—87°, which is probably *methyl butan-γ-one-aaβδδ-pentacarboxylate*, and also a very small quantity of an *ester*, $C_{12}H_{16}O_8$, m. p. 85° (*phenylhydrazone*, m. p. 110°), which is possibly *methyl hexan-βδ-dione-aγε-tricarboxylate*.

It is noteworthy that all the products obtained from ethyl malonate in the reaction under examination are methyl esters.

C. S.

Acidity of Derivatives of Ethyl Oxalacetate. Henri Gault (*Compt. rend.*, 1910, 150,1608—1610).—The ethyl esters of the following acids may be titrated by alkalis, using phenolphthalein as indicator, in cold alcoholic or acetone solutions; the results obtained enable the molecular weights to be determined with a fair degree of accuracy: oxalacetic, oxalosuccinic, α-oxaloglutaric, methylenebisoxalacetic, ethylidenebisoxalacetic, propylidenebisoxalacetic, heptylidenebisoxalacetic, *cyclo*pentan-βγ-dione-aδ-dicarboxylic, and the corresponding aε-di- and aδε-tri-carboxylic acids. The molecular weights thus determined agree with the accepted constitutions for these substances, but in the case of methyloxalosuccinic and α-oxalotricarballylic esters, the results are abnormally high. W. O. W.

Acidic Character of Ethyl Oxalacetate. Louis Jacques Simon (*Compt. rend.*, 1910, 150, 1760. Compare Abstr., 1904, i, 648; 1907, i, 963).—The author has already called attention to the acidic character of ethyl oxalacetate recently studied by Gault (preceding abstract). W. O. W.

Decomposition of Formaldehyde at a Red Heat. Armand Gautier (*Compt. rend.*, 1910, 150, 1725—1726. Compare this vol., ii, 607).—When a mixture of hydrogen and formaldehyde is passed through a porcelain tube heated to redness, the formaldehyde is decomposed in accordance with the equation: $CH_2O = CO + H_2$. If passed over iron at 650°, the gaseous product contains in addition 0·8% of methane. W. O. W.

Electro-syntheses. V. Sima M. Losanitsch (*Ber.*, 1910, 43, 1871—1874. Compare this vol., i, 1).—Methylal, when subjected to the silent electric discharge, yields carbon monoxide, methane, hydrogen, a small amount of unsaturated hydrocarbons, and large

quantities of aldehydes, which are polymerides of formaldehyde and acetaldehyde, namely, $C_3H_8O_3$, $C_7H_{18}O_6$, $C_8H_{18}O_5$, and $(C_3H_6O_2)_n$.

Acetal yields aldehyde compounds: $C_6H_{12}O_2$, b. p. 100—110°/16 mm.; $C_{16}H_{30}O_5$, b. p. 140—200°/16 mm., and $C_{14}H_{22}O_4$.

Methyl sulphide yields the compounds $C_5H_{12}S_4$, b. p. 45—50°/14 mm.; $C_7H_{16}S_5$, b. p. 80—90°/14 mm.; $C_5H_{12}S_4$, b. p. 120—140°/14 mm., and $C_7H_{14}S_6$, which are polymerides of formaldehyde and thioacetaldehyde.

*iso*Pentane and ammonia yield an oily *hydrocarbon*, C_nH_{2n}, and a *base*, $C_6H_{13}N$, which has b. p. 90—95°/14 mm.

Ether and ammonia yield a *base*, $C_9H_{17}ON_3$. J. J. S.

Injurious Action of the Sun's Rays on Acetone. Batik (*Chem. Zeit.*, 1910, **34**, 735).—When acetone is exposed to the direct rays of the sun, it is affected in such a way that it almost immediately decolorises permanganate. When kept overnight, however, it regains its ordinary properties. The direct rays of the sun are necessary for this effect, and their influence is not prevented by the use of coloured, light-absorbing flasks. According to the author the action only takes place in May and June to any extent; it has not been observed in April, August, or September. T. S. P.

Photochemical Synthesis of Carbohydrates from Carbon Monoxide and Water Vapour in the Absence of Chlorophyll; Photochemical Synthesis of Quaternary Compounds. Daniel Berthelot and Henri Gaudechon (*Compt. rend.*, 1910, **150**, 1690—1693).—Synthetical processes of the type occurring in plants may in some cases be effected by the aid of the quartz-mercury lamp. The following reactions have been studied from this point of view, and carried out through the agency of ultra-violet light: $CO + O \rightleftarrows CO_2$; $CO + H_2 \rightleftarrows H{\cdot}CHO$; $xCH_2O \rightleftarrows (CH_2O)_x$; $H_2 + O \rightleftarrows H_2O$. Formamide has been obtained by exposing a mixture of carbon monoxide and ammonia to ultra-violet light. W. O. W.

Carnine and Inosic Acid. IV. Franz Haiser and Franz Wenzel (*Monatsh.*, 1910, **31**, 357—361. Compare Abstr., 1909, i, 322, 540).—The pentose obtained from inosine and inosic acid has been regarded previously by the authors as *d*-lyxose, mainly on account of the m. p. of the phenylbenzylhydrazone. They have now prepared lyxose from galactonic acid by means of mercuric oxide by Guerbet's method, and find that its phenylbenzylhydrazone depresses the m. p. of that of the pentose 40°. The pentose, therefore, has been converted into the *p*-bromophenylhydrazone; this has m. p. 166°, corresponding with that of *l*-ribose-*p*-bromophenylhydrazone. The authors agree, therefore, with Levene that the pentose from inosine is *d*-ribose. C. S.

Identity of Crystallised Aloinose with *d*-Arabinose. Eugène Léger (*Compt. rend.*, 1910, **150**, 1695—1697. Compare this vol., i, 463).—Aloinose is shown to be identical with *d*-arabinose. Inasmuch as barbaloin and *iso*barbaloin yield the same products on hydrolysis, they would appear to be stereoisomeric glucosides. W. O. W.

*iso*Maltol. Arnold Backe (*Compt. rend.*, 1910, 151, 78—80).—The name iso*maltol* is suggested for the compound the preparation of which from bread or biscuits has already been described (this vol., i, 225). It is very stable, and forms crystals having the composition $C_6H_6O_3$; m. p. 98°. It forms a yellow solution in aqueous sodium carbonate, liberating carbon dioxide. The compound reduces Fehling's solution, and gives the iodoform reaction; the *benzoyl* derivative has m. p. 99°. The crystalline *copper* salt, $Cu(C_6H_5O_3)_2,H_2O$, is much more stable than the corresponding salt of maltol. The *methyl* derivative, obtained by the action of diazomethane, crystallises in tablets, m. p. 102°, subliming in long needles. *iso*Maltol also differs from maltol in not yielding acetic acid on hydrolysis, and in the formation of a yellow, crystalline *compound*, m. p. 138°, when treated with amyl nitrite. Phenylhydrazine brings about decomposition. The following constitution is suggested for *iso*maltol : $OH\cdot C\begin{matrix}CH{-}{-}O\\ CO\cdot CMe\end{matrix}CH$.

W. O. W.

Properties of Lintner's Soluble Starch. E. D. Clark (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, 7, lv—lvii).—The result of dialysing solutions of soluble starch, precipitating the solution left in the dialyser by means of alcohol and a drop of 10% sodium chloride solution, and examining both the precipitate and the solution leads the author to the conclusion that soluble starch carries associated with it certain amounts of dextrins with reducing properties, and that it can only be partially freed from these by dialysis or precipitation.

Soluble starch of low reducing power can be prepared in a few minutes by the following process: A thick starch paste made by pouring a suspension of 4 grams of potato starch in 15 c.c. of cold water into 200 c.c. of water at 95°, is cooled to 40°, and then mixed with 5 c.c. of filtered saliva and stirred rapidly. In two or three minutes the whole is liquefied, and is then poured into 95% alcohol and a drop of 10% sodium chloride solution added. The soluble starch is filtered quickly, dropped into a little boiling water to destroy ptyalin, and immediately cooled. The substance is readily soluble in water, whereas Lintner's starch is not. J. J. S.

Autoxidation of Ethyl Dialkylthiocarbamates. Otto Billeter (*Ber.*, 1910, 43, 1853—1857. Compare Delepine, this vol., i, 295).—Ethyl dimethylthiocarbamate and analogous esters fume and phosphoresce in contact with atmospheric oxygen, giving rise to a characteristic odour, analogous to that formed during the autoxidation of phosphorus. In closed vessels the phenomenon ceases after a short time, and is also inhibited by pressures of 5—10 atmospheres. The action is most pronounced in the presence of alkalis, and neither ozone nor hydrogen peroxide appears to be formed. In open vessels and under favourable conditions, the process continues until all the substance is used up.

The velocity of the absorption of oxygen remains constant until nearly the end of the operation, provided the pressure of the oxygen

is constant and that regular shaking is adopted. Toward the end the rate diminishes rapidly, then increases again, and becomes constant, but with a velocity some 1/100th of the original.

It is probable that the thiocarbamate first forms an unstable peroxide, which decomposes, yielding the carbamate, $NMe_2{\cdot}CO{\cdot}OEt$, and sulphur monoxide, and that the latter reacts with the alkali present, forming a thiosulphate. In most cases more than the theoretical amount of oxygen is absorbed, owing to the formation of sulphite and sulphate, and salts of an acid, $H_2S_3O_5$. This acid can be regarded as a mixed anhydride of sulphurous and thiosulphuric acid. The *sodium* salt, $Na_2S_3O_5,10H_2O$, forms definite crystals, and is oxidised by iodine to sodium trithionate: $Na_2S_3O_5 + H_2O + I_2 = Na_2S_3O_6 + 2HI$. Potassium disulphide, on the other hand, converts it into thiosulphate:

$$Na_2S_3O_5 + Na_2O + K_2S_2 = 2Na_2S_2O_3 + K_2S.$$

Methyl dimethylthiocarbamate, $NMe_2{\cdot}CS{\cdot}OMe$, is a colourless liquid, b. p. 68·2°/10 mm., m. p. 3·2°, and D_4^{15} 1·0773. The *ethyl* ester has b. p. 82·6°/10 mm., m. p. 14·3°, and D_4^{15} 1·0343; the *propyl* ester, b. p. 96·5—97·5°/12 mm., and D_4^{15} 1·0160; the iso*butyl* ester, m. p. 28·8°, and the iso*amyl* ester, $NMe_2{\cdot}CS{\cdot}OC_5H_{11}$, b. p. 119—119·5°/10 mm., and D_4^{15} 0·9688.

Methyl diethylthiocarbamate, $NEt_2{\cdot}CS{\cdot}OMe$, has b. p. 105·2—105·6°/10 mm., and D_4^{15} 1·0078.

Other sulphur compounds, such as ethyl carbamate, ethyl phenylethylcarbamate, ethyl thiocarbonate, and tetramethylcarbamide, do not appear to be capable of absorbing oxygen.

Tetramethylthiocarbamide, $CS(NMe_2)_2$, forms colourless crystals, m. p. 73·8°. J. J. S.

New Case of Spontaneous Oxidation with Phosphorescence. Marcel Delépine (*Compt. rend.*, 1910, **150**, 1607—1608. Compare this vol., i, 295).—The property of spontaneous phosphorescence exhibited by compounds containing the $S{\cdot}\dot{C}{\cdot}O{\cdot}$ group is shared by thiocarbonyl chloride. Substances containing the $O{\cdot}CS{\cdot}NH_2$ group, or the $\cdot S{\cdot}\dot{C}{:}O$ or $\cdot S{\cdot}\ddot{C}{\cdot}O\cdot$ groupings, are not phosphorescent. W. O. W.

Crystallography of the Salts of Methylguanidine. Arthur Schwantke (*Arch. Pharm.*, 1910, **248**, 390—397).—The crystallographic examination of the platinichloride and the aurichloride of the methylguanidine obtained by Schenck by the oxidation of γ-methylglycocyamidine (this vol., i, 546) proves the identity of these salts with the corresponding salts of the methylguanidine obtained by the oxidation of creatine or from methylamine and cyanamide. C. S.

Synthetical Homocholines. Fernand Malengreau and A. Lebailly (*Zeitsch. physiol. Chem.*, 1910, **67**, 35—41).—Several homocholines have been synthesised in order to compare them with neosine, which is also a homologue of choline, according to Kutscher and Ackermann (Abstr., 1908, i, 675).

γ-Homocholine (*γ-hydroxytrimethylpropylammonium chloride*),

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Cl,$$

obtained by heating trimethylenechlorohydrin with a 33% trimethylamine solution at 100° for six hours, forms large, colourless, prismatic crystals, which are deliquescent. The *hydroxide* forms a syrup, which slowly crystallises. The *aurichloride*, $C_6H_{16}ONAuCl_4$, forms glistening plates, m. p. 183° (corr.), and the *platinichloride*, $(C_6H_{16}ON)_2PtCl_6$, crystallises from 85% alcohol in characteristic, long, silky, orange-red needles, m. p. 227—228° (corr.). These salts are quite different from those of a γ-homocholine described by Schmidt and Partheil (Abstr., 1892, 950).

β - Hydroxytrimethylpropylammonium chloride (*β-homocholine*), $OH{\cdot}CHMe{\cdot}CH_2{\cdot}NMe_3Cl$, obtained by heating propylene chlorohydrin, $CH_2Cl{\cdot}CHMe{\cdot}OH$, with 33% alcoholic trimethylamine solution at 100° for six hours, forms extremely deliquescent crystals. The *hydroxide* is a syrup, and at 170—180° yields trimethylamine and the glycol. The *aurichloride*, $C_6H_{16}ONAuCl_4$, crystallises in glistening, golden-yellow plates, m. p. 195—196° (corr.). The *platinichloride*, $(C_6H_{16}ON)_2PtCl_6$, crystallises in orange-yellow, regular octahedra. The two isomeric bases are most readily distinguished by means of their characteristic platinichlorides.

An isomeric β-homocholine (*iso*propyleneneurine),

$$OH{\cdot}CH_2{\cdot}CHMe{\cdot}NMe_3Cl,$$

has been described by Morley (Abstr., 1881, 151). J. J. S.

Glycocyamine and Glycocyamidine. Martin Schenck (*Arch. Pharm.*, 1910, 248, 376—389).—The derivative obtained by the methylation of glycocyamidine, and regarded as δ-methylglycocyamidine by Korndörfer (Abstr., 1905, i, 29), is proved by oxidation by alkaline 5% potassium permanganate at 50—60° to be γ-methylglycocyamidine, $NH{:}C\begin{<}NH\text{--}CH_2\\NMe{\cdot}CO\end{>}$, since the products are oxalic acid and the same methylguanidine as is obtained by the oxidation of creatinine. A comparative experiment on the oxidation of creatinine by the preceding oxidising mixture shows that, not only methylguanidine, but also guanidine itself is formed. C. S.

Compounds of Amino-acids and Ammonia. VI. Peter Bergell and Theodor Brugsch (*Zeitsch. physiol. Chem.*, 1910, 67, 97—103. Compare Bergell and Wülfing, this vol., i, 304).—*dl*-Leucinamide is fermented by liver extract, and yields *d*-leucinamide; the same type of reaction is brought about by kidney extract.

dl-Alanimide also undergoes asymmetric fermentation to a certain extent when left in contact with kidney extract or meat extract.

Löb and Higuchi's placenta powder is without action on leucinamide, whereas placenta magma ferments both leucinamide and alanimide, and yields the active compounds.

dl-Leucinamide gives an onion-red coloration with dilute sodium hydroxide and a drop of very dilute copper sulphate solution; the addition of more copper sulphate produces a violet-red coloration, and with concentrated solutions a heavy precipitate is formed. When dissolved in dilute hydrochloric acid, neutralised with *N*-sodium

hydroxide, filtered, and evaporated under reduced pressure, flat, onion-red prisms are obtained; they melt at 222—223° (corr., decomp.), and contain C 29·69, H 8·14, N 17·25, and Cu 19·7%. J. J. S.

Diazoaminotetrazolic Acid. Karl A. Hofmann and Heinrich Hock (*Ber.*, 1910, 43, 1866—1871. Compare this vol., i, 232, 446).—Sodium nitrite in the presence of acetic acid reacts in the cold with aminoguanidine dinitrate, yielding a *sodium* salt, $C_2H_2N_{11}Na,2H_2O$, which is regarded as the salt of *diazoaminotetrazolic acid*,

$$N_3\cdot C(:NH)\cdot N:N\cdot NH\cdot C(:NH)\cdot N_3.$$

The acid crystallises in doubly refracting, glistening lamellæ containing $1H_2O$ after drying under reduced pressure over phosphoric oxide. It is a strong tribasic acid.

The *disodium* salt, $C_2HN_{11}Na_2,H_2O$, crystallises in orange-red prisms, and yields yellow aqueous solutions which are slightly acid. The *barium* salt, $(C_2N_{11})_2Ba_3.8H_2O$, forms sulphur-yellow plates, which rapidly effloresce. The *ammonio-copper* salt, $(C_2N_{11})_2Cu_3,2NH_3$, crystallises in dark green, pleochroic plates; when mixed with potassium chlorate and gum, it forms a powerful detonator. The acid and all the salts explode when heated.

The *disilver* salt, $C_2HN_{11}Ag,H_2O$, is obtained by washing the precipitated salt with dilute ammonia and then with dilute nitric acid; if the washing with nitric acid is omitted, the *tertiary silver* salt, $C_2N_{11}Ag_3$, is obtained.

The acid and its salts are stable towards nitrous acid, but are decomposed by stannous chloride and hydrochloric acid, yielding aminotetrazole and tetrazylhydrazine (Thiele and Marais, Abstr., 1893, i, 441): $HN_4C\cdot N:N\cdot NH\cdot CN_4H + 4H = HN_4C\cdot NH\cdot NH_2 + NH_2\cdot CN_4H$.

This supports the constitution ascribed to the acid, and further confirmation is obtained by the synthesis of the acid by partial diazotisation of aminotetrazolic acid.

When boiled with acidified water, the sodium salt yields nitrogen and cyanogen, together with aminotetrazole, a decomposition analogous to that of diazoaminotetrazole to aminotetrazole, nitrogen, and cyanogen. With permanganate and dilute sulphuric acid, more than seven atoms of oxygen are taken up by the acid. J. J. S.

Alkyl Derivatives of Sodium and Their Reactions with Ethers. Paul Schorigin (*Ber.*, 1910, 43, 1931—1938. Compare Abstr., 1907, i, 753; 1908, i, 867, 881).—The reaction between sodium and mercury diethyl takes place in the following stages at 100—170°: $Hg(C_2H_5)_2 + 2Na = Hg + 2C_2H_5Na$, $2C_2H_5Na + 2Hg = 2NaHg + C_2H_4 + C_2H_6$ (compare Buckton, *Annalen*, 1859, 112, 220), as equal volumes of ethylene and ethane are formed during the reaction. Butane is not formed (compare Krafft and Göttig, *Ber.*, 1888, 21, 3180). When sodium reacts with mercury diethyl in a solution of light petroleum, ether, or hexane, black, spontaneously inflammable incrustations are formed on the surface of the sodium, and the liquid remains clear; when ether is used as solvent, a voluminous precipitate of sodium ethoxide is formed, according to the equation: $C_2H_5Na + (C_2H_5)_2O = C_2H_5ONa + C_2H_6 + C_2H_4$. It is possible that an

additive compound, OEt_3Na, is first formed, and that this subsequently decomposes. Other ethers react in a similar manner. Sodium *iso*amyl (from sodium and mercury di*iso*amyl) and ethyl ether yield sodium ethoxide and not sodium *iso*amyl oxide. Sodium ethyl and phenetole yield sodium phenoxide. J. J. S.

Secondary Action of Aluminium Chloride on Aromatic Chloro-compounds. James Lavaux and Maurice Lombard (*Bull. Soc. chim.*, 1910, [iv], 7, 539—542).—Friedel and Crafts explained the formation of dimethylanthracene in the action of benzyl chloride on toluene in presence of aluminium chloride as due to the occurrence of some xylyl chloride in the benzyl chloride used, but this explanation is invalid, since if xylyl chloride yields dimethylanthracene under these conditions, benzyl chloride should yield anthracene, and further it has been shown that benzyl chloride, free from xylyl chloride, still furnishes dimethylanthracene. Re-investigation of the products formed in this type of reaction indicates that two reactions may occur, represented by the following equations: $R{\cdot}Me + AlCl_3 = R{\cdot}AlCl_2 + MeCl$ and $R{\cdot}CH_2Cl + AlCl_3 = R{\cdot}AlCl_2 + CH_2Cl_2$. The methyl chloride thus formed reacts with aromatic hydrocarbons to form polymethylbenzenes, and the methylene chloride condenses with aromatic hydrocarbons, or in their absence with the aromatic chloro-compounds, to give anthracenes, the latter being always a secondary reaction. In support of these views, the following results of condensations in presence of aluminium chloride are given. Benzyl chloride reacts (1) with benzene to furnish diphenylmethane and anthracene; (2) with toluene to give phenyltolylmethane and a mixture of 1 : 6- and 2 : 7-dimethylanthracenes. Xylyl chloride condenses with toluene to give ditolylmethane and a mixture of 1 : 6- and 2 : 7-dimethylanthracenes. Benzyl chloride alone condenses to form "benzylene resin," $(C_6H_5{\cdot}CH)_n$, which on distillation yields some anthracene. Xylyl chloride also yields "benzylene resin," but in addition small quantities of the 1 : 6- and 2 : 7-dimethylanthracenes. T. A. H.

Compounds of Trinitrobenzene with Hydrazine, Phenylhydrazine, and Azobenzene: The Side Valency of the Nitro-group. Karl A. Hofmann and H. Kirmreuther (*Ber.*, 1910, 43, 1764—1767).—Trinitrobenzene forms well-characterised crystalline compounds with hydrazine, phenylhydrazine, and azobenzene, of which the two former are deep red and the third is orange in colour. These are regarded as true molecular compounds, as they are quantitatively decomposed by solvents, for example, water, into their components.

The hydrazine salts of the nitrophenols are lighter and more faintly coloured than trinitrobenzene hydrazine. Trinitro-xylene and trinitromesitylene do not form similar coloured molecular compounds with hydrazine; trinitrotoluene yields a red solution, but the compound with hydrazine could not be obtained crystalline.

Trinitrobenzene-dihydrazine, $C_6H_3(NO_2)_3,2NH_2{\cdot}NH_2$, forms crystals, m. p. 122—123° (decomp.), which are deep red by transmitted light, but have a metallic green lustre.

Trinitrobenzene-phenylhydrazine, $C_6H_3(NO_2)_3,N_2H_3Ph$, forms dark

red, long, flat prisms, which sinter at 75—80° and decompose with a slight explosion.

Ditrinitrobenzeneazobenzene, $[C_6H_3(NO_2)_3]_2Ph{\cdot}N_2{\cdot}Ph$, forms orange, four-sided plates, m. p. 131—132°, to a red liquid, which explodes when superheated. E. F. A.

Hydro-aromatic Substances. Edward Divers, Arthur W. Crossley, William H. Perkin, Martin O. Forster, and Henry R. Le Sueur (*Brit. Assoc. Report*, 1909, 145—147).—This report deals with the nitro-derivatives of *o*-xylene, the synthesis of *iso*phorone and its homologues, and the constitution of Harries and Antoni's "1 : 1-dimethyl-$\Delta^{2,5}$-*cyclo*hexadiene." E. H.

Two Solid Polymeric Nitroso-ψ-cumenes. Eugen Bamberger (*Ber.*, 1910, 43, 1842—1849. Compare Cain, Trans., 1908, 93, 683).—ψ-Cumidine, when oxidised at 0° to 5° with a neutral solution of Caro's reagent, yields a mixture of two solid *nitroso-ψ-cumenes* (5-*nitroso*-1 : 2 : 4-*trimethylbenzene*, $NO{\cdot}C_6H_2Me_3$). The crude product is purified by treatment with cold very dilute hydrochloric acid, and then by steam distillation. The colourless crystals are obtained when the hot alcoholic solution is rubbed with a glass rod. If the solution is left without stirring or rubbing, green crystals, mixed with a few colourless crystals, m. p. 65°, are obtained. The green compound is metastable, and passes more or less readily into the colourless. The green compound can also be prepared by melting the colourless form and cooling the melt rapidly by means of cold water. It has a bluish-green colour, melts at 45—46°, and is much more readily soluble than the colourless modification in most organic solvents.

Other nitroso-derivatives which form green crystals appear to exist in the one form only. The author has not succeeded in preparing Cain's colourless *p*-nitrosoacetanilide (*loc. cit.*). The green form has m. p. 179·5—180·5° (corr.).

ψ-Cumylhydroxylamine, $C_6H_2Me_3{\cdot}NH{\cdot}OH$, crystallises in glistening, colourless, flat needles, m. p. 103·5—104°, and yields 1 : 2 : 5-trimethylquinol when left in contact with dilute sulphuric acid for several days (compare Abstr., 1903, i, 557). J. J. S.

Isomorphous Sulphonic Derivatives of Benzene. Henry A. Miers, Henry E. Armstrong, William J. Pope, and William P. Wynne (*Brit. Assoc. Report*, 1909, 141—143).—This report deals with the crystallographic relationships of *p*-dibromobenzene-sulphonyl chloride and bromide, -sulphonanilide, and ethyl sulphonate, 1-chloro-4-iodobenzene-3-sulphonyl chloride and bromide, and *p*-di-iodobenzene-sulphonyl chloride towards each other and towards benzene, with especial reference to the Pope-Barlow theory. E. H.

Reaction between Organic Magnesium Compounds and Dibromoanthracene Tetrabromide. Wladimir Naumoff (*J. pr. Chem.*, 1910, [ii], 82, 181—182).—Magnesium phenyl, tolyl, mesityl and ethyl bromides react with dibromoanthracene tetrabromide in ethereal solution with the formation of dibromoanthracene, simply withdrawing four atoms of bromine. T. S. P.

9 : 9-Dichlorofluorene and its Conversion into Bidiphenylene-ethene. Julius Schmidt and Hans Wagner (*Ber.*, 1910, 43, 1796—1802).—Fluorenone, when heated with phosphorus pentachloride, is converted into 9 : 9-*dichlorofluorene*, the colour change from glistening yellow, $>CO$, to the colourless, $>CCl_2$, group being very marked. The chlorine can be eliminated from this compound by means of copper powder, forming first dichloro-*s*-bidiphenylene-ethylene, which is colourless, and then bidiphenylene-ethylene,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C{:}C\!<\!\!\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$$

(compare Graebe, Abstr., 1896, i, 566), which is intense red. It is conveniently prepared by this reaction. 9 : 9-Dichlorofluorene reacts with phenylhydrazine, hydroxylamine, etc., similarly to fluorene, and gives the same products, but more readily.

Dichlorofluorene forms colourless quadrants, m. p. 99°, and dissolves in concentrated sulphuric acid with a violet coloration.

Dichloro-*s*-bidiphenylene-ethane, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CCl\cdot CCl\!<\!\!\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$, separates in colourless crystals, m. p. 230—232°.

Fluorenone-p-*nitrophenylhydrazone*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C{:}N\cdot NH\cdot C_6H_4\cdot NO_2$, prepared either from fluorenone or from dichlorofluorene, crystallises in orange-yellow needles, m. p. 269°. E. F. A.

Compounds which cause the Red Coloration of Aniline. I. Effect of Oxygen and Ozone, and the Influence of Light in the Presence of Oxygen. Harry D. Gibbs (*Philippine J. Sci.*, 1910, 5, 9—16).—Bottles containing aniline are placed in sunlight and constantly agitated for about one month. The stoppers are removed from time to time, and the air over the liquid changed. The deep red liquid is then dissolved in very dilute sulphuric acid; the insoluble portion contains 2 : 5-dianilinoquinone. Without being filtered, the sulphuric acid solution is extracted with ether. The ethereal extract contains dianilinoquinone, dianilinoquinoneanil, and azobenzene. Another portion of the coloured aniline is poured into 50% acetic acid; when cold, the solution deposits the characteristic twinned crystals of azophenine.

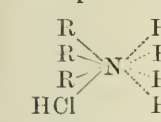
Dry purified aniline, free from sulphur compounds, can be kept unchanged for two months in an atmosphere of an inert gas. In dry, purified oxygen, the coloration of the aniline proceeds slowly in darkness and very rapidly in sunlight. The presence of moisture or impurities is not necessary for the production of the colour. In contact with ozonised oxygen, aniline is instantly coloured, rapidly becomes dark red, and evolves carbon dioxide; ultimately the liquid sets to a crystalline mass of dianilinoquinoneanil. C. S.

Addition of Hydrogen Chloride to Substituted Anilines at Low Temperatures. Antoni von Korczyński (*Ber.*, 1910, 43, 1820—1824. Compare Abstr., 1909, i, 123; Kaufler and Kunz, *ibid.*, 136, 556).—The following compounds have been isolated at

$-75°$: With 8HCl, *p*-nitrosodimethylaniline; with 6HCl, *p*-nitrosoaniline; with 5HCl, *m*-nitrodimethylaniline; with 4HCl, 2 : 4-dinitroaniline, 3 : 5-dinitroaniline, 4 : 6-dibromo-2-nitroaniline; with $3\frac{1}{2}$HCl, 2 : 6-dinitroaniline; with 3HCl, aniline, diphenylamine, 4 : 6-dichloro-2-nitroaniline, 2 : 6-dichloro-4-nitroaniline, 2 : 6-dibromo-4-nitroaniline, *p*-nitrodimethylaniline, *o*-, *m*-, *p*-aminobenzoic acids; with $2\frac{1}{2}$HCl, 2 : 4-dichloroaniline, dibromo-*o*-toluidine, trichloroaniline; with 2HCl, *p*-toluidine, *o*-, *m*-, *p*-chloroanilines, *o*-, *m*-, *p*-bromoanilines, *p*-iodoaniline, 3 : 5-dichloroaniline, 3 : 5-dibromoaniline, dibromo-*p*-toluidine, 3 : 5-dichloro-2 : 4 : 6-tribromoaniline, 4-bromo-2 : 6-dinitroaniline, carbamide, thiocarbamide; with 1HCl, 6-bromo-2 : 4-dinitroaniline.

Trinitroaniline does not combine with hydrogen chloride.

The maximum number of molecules of hydrogen chloride is 5, except in the case of the nitroso-derivatives, where the oxygen atom also probably adds on hydrogen chloride. This points to the co-ordinate number 8, and the annexed type of formula is suggested.



It is noticed that monohalogen derivatives of aniline add on 2HCl, and that the introduction of a second halogen atom into the ortho- or para-position can increase the additive capacity of the amine. The introduction of 3 or even 5 halogen atoms does not prevent the formation of hydrochlorides. The introduction of a second nitro-group into the molecule of nitroaniline has much the same effect as the introduction of a second halogen atom into a monohalogen derivative of aniline. Two nitro-groups in the ortho-position with respect to the amino-group are not so favourable to addition as the same groups when in 2 : 4- or 3 : 5-positions, and the presence of three nitro-groups can prevent the formation of an additive compound.

The acid sulphate of a base as a rule combines with two molecules of hydrogen chloride less than the base itself; thus *p*-nitrosodimethylaniline sulphate forms the colourless *compound*,

$$NO\cdot C_6H_4\cdot NMe_2,H_2SO_4,6HCl.$$

Naphthaquinoline forms a compound with 5HCl, and its acid sulphate a compound with 3HCl. Quinoline acid sulphate also combines with 3HCl. Ammonium chloride, ammonium sulphate, and hydrazine sulphate do not combine with hydrogen chloride.

Most of the compounds mentioned are colourless, a few have a pale yellow colour, and the compound from nitrosoaniline is yellow.

J. J. S.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. Frederic S. Kipping, Kennedy J. P. Orton, Siegfried Ruhemann, Arthur Lapworth, and John T. Hewitt (*Brit. Assoc. Report*, 1909, 147—149).—This report [with W. C. Evans and W. J. Jones] deals with the transformation of *p*-chloroacetylchloroaminobenzene into dichloroacetanilide. E. H.

Some New Thorium Salts. Georges Karl (*Ber.*, 1910, 43, 2068—2070).—*Thorium picrate*, $Th(C_6H_2N_2O_7)_4,10H_2O$, separates as

an oil, which solidifies to a yellow, hard, crystalline mass, when ammonium picrate is added to a hot aqueous solution of thorium nitrate. Small, yellow needles, m. p. 52—53°; explodes on heating with the bare flame. It can be dehydrated at 105°, and then forms a vitreous, yellow mass, which is still solid at 100°. At 25°, 100 c.c. of water dissolve 0·3052 gram of the hydrated picrate.

Thorium hippurate, $(COPh{\cdot}NH{\cdot}CH_2{\cdot}CO_2)_4Th$, is formed from thorium nitrate and ammonium hippurate. White, crystalline powder, slightly soluble in water. One hundred c.c. of water dissolve 0·0318 gram at 25°.

Basic thorium chloroacetates are obtained when freshly-prepared basic thorium carbonate is added to the various chloroacetic acids. *Basic thorium monochloroacetate*, $(CH_2Cl{\cdot}CO_2)_2Th(OH)_2,H_2O$; small, white needles from alcohol. *Basic thorium dichloroacetate*,

$$(CHCl_2{\cdot}CO_2)_2Th(OH)_2;$$

small prisms from alcohol. *Basic thorium trichloroacetate*,

$$(CCl_3{\cdot}CO_2)_2Th(OH)_2;$$

small, shining, and transparent octahedra, which contain water of crystallisation, but effloresce on exposure to the air. T. S. P.

Behaviour of 3-Nitro-*p*-cresol towards Sulphuric Acid. II. Gustav Schultz and Oskar Löw (*Ber.*, 1910, **43**, 1899—1902. Compare Abstr., 1909, i, 222).—When 3-nitro-*p*-cresol is added slowly to concentrated sulphuric acid on the water-bath, the product is the same as that obtained by the action of cold fuming sulphuric acid, namely, *β*-acetylacrylic acid. By-products of the reaction are a *substance* (*α*-nitro-*β*-acetylacrylic acid?), m. p. 206—207° (decomp.), and *ammonium 3-nitro-p-cresol-5-sulphonate*, which is reduced by stannous chloride and hydrochloric acid to the corresponding *amino*-compound. C. S.

Action of Nitroso-derivatives on Unsaturated Compounds. Angelo Angeli, Luigi Alessandri, and Raffaello Pegna (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 650—659).—The authors have investigated the action of nitrosobenzene on anethole, *iso*safrole, safrole, and ethyleugenol. In the first two cases no definite reaction-product was isolated. When a mixture of safrole and nitrosobenzene is kept in the dark for four or five days at the ordinary temperature, a *substance*, crystallising in golden-yellow needles, m. p. 193°, is obtained, in addition to azoxybenzene. The compound has the formula $C_{16}H_{13}O_3N$, and the authors ascribe to it the constitution

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}NOPh.$$

It yields nitrosobenzene when exposed to light, or to the action of oxidising agents, and, when it is oxidised with potassium permanganate in alkaline solution, piperic acid is formed. By the action of dilute mineral acids, it is converted into an isomeric *compound*, which has m. p. 195°, and the authors regard it as a Schiff's base; it is a yellow powder, is soluble in alkalis, and yields a *sulphate*, m. p. 174°. It forms a benzoyl derivative, $C_{20}H_{15}O_3N$, m. p. 229°, identical with that obtained by the action of benzoyl chloride on *p*-aminophenol. The base is also acted on readily by hydroxylamine, three oximes of the

formula $C_{10}H_9O_3N$ being produced. The *α-oxime* crystallises in long, thin needles, m. p. 195°; the *β-oxime* forms lustrous laminæ, m. p. 191°, and the *γ-oxime*, short needles, m. p. 155°. With benzoyl chloride both the *β*- and *γ*-oxime yield the same *benzoyl* derivative, $C_{17}H_{13}O_4N$, m. p. 175°. All three compounds show the behaviour of oximes. When they are boiled with dilute acid, piperonylacraldehyde is formed; this substance is, however, best prepared by the action of amyl nitrite. Whether prepared in this way or from piperonal by the method of Ladenburg and Scholtz, it has m. p. 84°, although these authors gave (Abstr., 1895, i, 42) m. p. 70°. Phenylhydroxylamine reacts with the aldehyde, forming the same compound of m. p. 193° as is obtained from safrole and nitrosobenzene.

The action of nitrosobenzene on ethyleugenol is similar to its action on safrole: a *compound*, $C_{18}H_{19}O_3N$, is formed, which crystallises in small, yellow needles, m. p. 155°. R. V. S.

Phenanthrene Series. XXVIII. Bromination and Nitration of 9-Hydroxyphenanthrene. Julius Schmidt and Otto Sroun (*Ber.*, 1910, 43, 1802—1807. Compare Abstr., 1909, i, 134; this vol., i, 312).—By the action of bromine in carbon disulphide solution, 9-hydroxyphenanthrene yields a dibromo-derivative containing one bromine atom in position 3 in the nucleus, since it yields 3-bromophenanthraquinone on oxidation with chromic acid. The other bromine atom is in position 9 or 10, and the compound has the formula $C_6H_3Br{<}\begin{matrix}C(OH)\\ \|\\ CBr\end{matrix}{>}C_6H_4$ or $C_6H_3Br{<}\begin{matrix}CBr\\ \|\\ C(OH)\end{matrix}{>}C_6H_4$. The same compound is obtained on brominating 9-acetoxyphenanthrene, and this method is preferable.

Before nitration of 9-hydroxyphenanthrene, the hydroxyl group has to be protected by acetylation, and certain further precautions must be observed to prevent oxidation. A dinitroacetoxy-compound is obtained containing one nitro-group in position 3, and the other is either 9 or 10; it yields 3-nitrophenanthraquinone on oxidation.

3 : 9-*Dibromo*-10-*hydroxyphenanthrene* has m. p. 135°; 9-*acetoxyphenanthrene* has m. p. 77°; 3 : 9-*dibromo*-10-*acetoxyphenanthrene*, prepared by acetylation of the dibromo-derivative, crystallises in colourless needles, m. p. 177°.

3 : 9-*Dinitro*-10-*acetoxyphenanthrene* is a yellow powder, m. p. 137—138°. E. F. A.

Behaviour of Aromatic Disulphides at High Temperatures. Oscar Hinsberg (*Ber.*, 1910, 43, 1874—1879).—When the simple aromatic disulphides are heated in a sealed tube at 240—280° they decompose into a mixture of the monosulphide and trisulphide. With more complex disulphides, other disturbing reactions take place, which may completely suppress the simple wandering of the sulphur atom.

Phenyl disulphide at 280° gives a mixture of monosulphide and trisulphide in the proportions required by the equation: $2S_2Ph_2 = SPh_2 + S_3Ph_2$. α-Naphthyl disulphide at 260—270° gives a mixture of the mono- and tri-sulphide. 4 : 4′-Dithioacetanilide at 180° gives a mixture of the three isomeric dithioacetanilides. At 240—260° a

mixture is obtained, from which it is difficult to separate the constituents; thus far the presence of 4 : 4′-thioacetanilide has been proved.

Dithiosalicylic acid [*o*-disulphidobenzoic acid, $S_2(C_6H_4\cdot CO_2H)_2$] at 280° gives a mixture containing the corresponding monosulphide, 2 : 2′-dicarboxydiphenyl sulphide (this vol., i, 261), and the thioanhydride of trithiosalicylic [trisulphidobenzoic] acid, which is formed instead of the expected *o*-trisulphidobenzoic acid. The dicarboxydiphenyl sulphide also loses carbon dioxide to some extent, with the formation of phenyl-2-carboxyphenyl sulphide. *o-Trisulphidobenzoic acid thioanhydride*, $CO\cdot C_6H_4\cdot S_3\cdot C_6H_4\cdot CO\cdot S$, forms light yellow needles, m. p. 75—76°, soluble in chloroform, insoluble in sodium carbonate or cold sodium hydroxide. It slowly dissolves in warm sodium hydroxide, and the addition of hydrochloric acid to the solution precipitates *o-trisulphidobenzoic acid*, $S_3(C_6H_4\cdot CO_2H)_2$, colourless flakes, difficultly soluble in all solvents, m. p. about 300°. In the thioanhydride, the middle ring is a 10-atom one.

Dimethyl *o*-disulphidobenzoate at 260—280° gives the dimethyl ester of 2 : 2-dicarboxydiphenyl sulphide; at the same time a wandering of the methyl group takes place with the formation of *o*-methylthiolbenzoic acid, as indicated by the scheme:

$$S_2(C_6H_4\cdot CO_2Me)_2 \rightarrow 2SMe\cdot C_6H_4\cdot CO_2H.$$

T. S. P.

Basic Properties of Sulphoxides and their Tautomerism. Emil Fromm and G. Raiziss (*Annalen*, 1910, **374**, 90—105).—Sulphides in which the sulphur is combined with a methyl or methylene group combine with halogens, forming dihalogenides; if, however, the sulphur is united directly with aromatic groups on both sides, dihalogenides are not formed. An attempt to ascertain the behaviour towards halogens of a sulphide containing the sulphur united with a –CH group was unsuccessful; the substance investigated, namely, the *p*-tolyl mercaptal of benzaldehyde,

$$CHPh(S\cdot C_6H_4Me)_2,$$

when acted on by bromine is decomposed with the formation of tolyl disulphide.

Analogously, when a sulphoxide containing a sulphoxy-group adjacent to a methyl or methylene group is treated with hydrogen bromide, it yields a dibromide, but if the sulphoxy-group is united to two aromatic groups, as in ditolyl sulphoxide, $SO(C_6H_4Me)_2$, the sulphoxide is not attacked by hydrogen bromide.

Di-p-tolyldithioethane, $C_2H_4(S\cdot C_6H_4Me)_2$, is formed by the interaction of *p*-thiocresol and ethylene bromide in an alcoholic solution of sodium hydroxide; it crystallises in transparent leaflets, m. p. 80°, and when oxidised with nitric acid, chromic acid, or hydrogen peroxide yields the corresponding *disulphoxide*, $C_{16}H_{18}O_2S_2$, which crystallises in silvery, white leaflets, m. p. 166° (decomp.). The following compounds are obtained by suitable methods from the dithio-compound by treatment with chromic acid or nitric acid: p-*tolylsulphone*-p-*tolylsulphoxyethane*, $C_6H_4Me\cdot SO_2\cdot CH_2\cdot CH_2\cdot SO\cdot C_6H_4Me$, long, colourless

needles, m. p. 148°; *di*-p-*tolylsulphonethane*, $C_2H_4(SO_2{\cdot}C_7H_7)_2$, long, glistening, transparent crystals, m. p. 199—200°; *dinitrodi*-p-*tolylsulphonethane*, $C_{16}H_{16}O_8N_2S_2$, long, pale yellow needles, m. p. 228°; *tetranitrodi*-p-*tolylsulphonethane*, $C_{16}H_{14}O_{12}N_4S_2$, yellow leaflets, m. p. above 300°.

A solution of di-*p*-tolyldithioethane in chloroform, when treated with bromine at 0°, yields the *tetrabromide*, $C_2H_4(SBr_2{\cdot}C_6H_4Me)_2$, obtained as small, glistening crystals, which appear yellowish-red by transmitted light and dark red by reflected light, m. p. 68—69°; it is so unstable that it cannot be recrystallised, and is decomposed by atmospheric moisture. The tetrabromide is converted by water at 0° into the di-*p*-tolylsulphoxyethane just described, and can be regenerated from the latter substance by treatment with hydrogen bromide. On the other hand, di-*p*-tolylsulphoxyethane is converted by bromine in chloroform into the *tetrabromide*, $C_{16}H_{18}O_2Br_4S_2$, which crystallises in red prisms, m. p. 96°.

Di-p-*tolyldithioethane di-iodide*, $C_{16}H_{18}I_2S_2$, is obtained by treating ditolyldithioethane (1 part) with iodine (1 part) in hot glacial acetic acid for a short time; it forms steel-blue needles, m. p. 83°. The *tetra-iodide*, $C_{16}H_{18}I_4S_2$, obtained by using iodine (2 parts) and heating the solution to 120° for about three hours, crystallises in wine-red leaflets, m. p. 88°.

Benzyl sulphide dibromide, $(CH_2Ph)_2SBr_2$, is obtained by acting on benzyl sulphide with a solution of bromine in chloroform at 0°, or by treating benzyl sulphoxide with hydrogen bromide; it forms yellowish-red crystals, m. p. 54°.

The p-*tolylmercaptal* of benzaldehyde, $C_{21}H_{20}S_2$, formed by the condensation of benzaldehyde and *p*-thiocresol under the influence of hydrogen chloride, crystallises in long prisms, m. p. 79°; it is oxidised by potassium permanganate, yielding *di*-p-*tolylsulphonephenylmethane*, $C_{21}H_{20}O_4S_2$, which forms stout, pointed plates, m. p. 163°.

The p-*tolylmercaptal* of acetone, $C_{17}H_{20}S_2$, is similarly prepared; it forms needles, m. p. 66°. W. H. G.

Active Pinonic and Pinic Acids. Philippe Barbier and Victor Grignard (*Bull. Soc. chim.*, 1910, [iv], 7, 548—557).—A detailed account of work already published (Abstr., 1908, i, 852), showing that Tiemann's *l*-pinonic acid (Abstr., 1896, i, 308) is not identical with the true *l*-pinonic acid derived from *l*-pinene. It is pointed out further that the *iso*propylheptanonolide derived from Tiemann's acid is not identical with that obtained from true *l*-pinonic acid, and since the structure of the *iso*propylheptanonolide does not permit of *cis-trans*-isomerism, it follows that Tiemann's acid cannot be a *cis-trans*-isomeride of true *l*-pinonic acid. It is suggested that Tiemann's acid should be called campholonic acid, and that the acid obtained by the same author by the oxidation of β-campholenic acid should be named β-campholonic acid.

l-Pinonic acid, crystallised from water over sulphuric acid, forms large, monoclinic prisms [$a:b:c=0{\cdot}5782:1:0{\cdot}6216$; $\beta = 105°$]. On treatment with sulphuric acid, it yields 1-iso*propylheptanonolide*,

$COMe\cdot CH_2\cdot CH_2\cdot CH<\begin{matrix}CMe_2\cdot O\\ |\\ CH_2-CO\end{matrix}$, m. p. 47—48°, $[\alpha]_D$ − 57·45° in alcohol, which separates in colourless, slender needles by addition of light petroleum to its solution in ether. On oxidation with sodium hypochlorite, *l*-pinonic acid furnished *d*-pinic acid, $[\alpha]_D$ +70·10°, and a second substance, which decomposes on distillation and may be a mixture of *cis*- and *trans*-isomerides. *d*-Pinonic acid, obtained by oxidising *d*-pinene from myrtle oil, furnishes *d*-iso*propylheptanonolide*, m. p. 47°, $[\alpha]_D$ +57·88°, and on oxidation *l*-pinic acid, m. p. 135°, which crystallises in small needles. A fused mixture of equal quantities of the two pinic acids gives *r*-pinic acid, m. p. 101—102°. In the preparation of both *l*- and *d*-pinonic acids some *r*-pinonic acid is also formed. T. A. H.

New Synthesis of Aromatic Carboxylic Acids from Hydrocarbons. II. Paul Schorigin (*Ber.*, 1910, 43, 1938—1942. Compare Abstr., 1908, i, 886).—An examination of the gaseous products formed by the action of dry carbon dioxide on a mixture of benzene, sodium wire, and mercury diethyl proves that the reaction proceeds in the stages: (1) $HgEt_2 + 2Na = Hg + 2NaEt$; (2) $C_6H_6 + C_2H_5Na = C_6H_5Na + C_2H_6$, and (3) $C_6H_5Na + CO_2 = C_6H_5\cdot CO_2Na$, as the proportion of ethane to ethylene is much greater (12 : 1) than is obtained by the action of sodium on mercury diethyl (this vol., i, 547). Benzoic acid can also be obtained by substituting sodium *iso*amyl for sodium ethyl, but the yield is not good.

The following acids have been synthesised by the action of carbon dioxide on sodium, mercury diethyl, and the respective hydrocarbon: *o*-Tolylacetic acid and *p*-tolylacetic acid from *o*- and *p*-xylenes, 3 : 5-dimethylphenylacetic acid from mesitylene, diphenylacetic acid from diphenylmethane, and *p*-homocouminic acid from *p*-cymene. The yield is poor in each case.

Thiophen-α-carboxylic acid is formed from thiophen, and the yield is somewhat better, 7 grams from 50 grams of thiophen. J. J. S.

Action of Pyridine on 2-Chloro-3 : 5-dinitrobenzoic Acid. Theodor Zincke (*J. pr. Chem.*, 1910, [ii], 82, 17—23. Compare this vol., i, 585).—When a mixture of pyridine and 2-chloro-3 : 5-dinitrobenzoic acid is kept for some hours, and is then heated for a short time on the water-bath, the *betaine*, $\begin{matrix}C_6H_2(NO_2)_2\cdot CO\\ |\\ C_5NH_5-\!\!-\!\!-O\end{matrix}$, m. p. 186—188° (decomp.), is formed. It separates from water in colourless, rhombic plates, yields 3 : 5-*dinitro*-2-*anilinobenzoic acid*, m. p. 214°, or the corresponding *toluidino*-derivative, m. p. 228°, by heating with aniline or *p*-toluidine in glacial acetic acid, and the *methyl* ester, m. p. 128°, or the *ethyl* ester, m. p. 97°, of dinitrosalicylic acid by treatment with methyl or ethyl alcohol at 100°. The action of 2*N*-sodium hydroxide on an aqueous solution of the betaine, which is subsequently acidified, leads to the formation of a reddish-brown, crystalline *substance*, $C_{12}H_9O_7N_3,H_2O$, m. p. 135—140° (decomp.), which regenerates the betaine by heating with hydrogen chloride in glacial acetic acid, yields

3 : 5-dinitro-2-aminobenzoic acid by treatment with boiling glacial acid and concentrated hydrochloric acids, and forms the dianilide, NPh:CH·CH:CH·CH:CH·NHPh (Abstr., 1904, i, 921), and dinitroaminobenzoic acid when boiled with an excess of aniline and a little alcohol. The substance is, therefore,

$CO_2H·C_6H_2(NO_2)_2·N:CH·CH:CH·CH:CH·OH$

or $CO_2H·C_6H_2(NO_2)_2·N:CH·CH:CH·CH_2·CHO$. C. S.

Lactonoid Anhydrides of Acylated Amino-acids. IV. Behaviour of Hippuric Acid, Hippuramide, and *r*-Acetylalanine towards Dehydrating Agents. Ernst Mohr and Fr. Stroschein (*J. pr. Chem.*, 1910, [ii], 82, 60—64).—A continuation of the preceding paper (this vol., i, 483). Attempts to prepare the lactonoid anhydride of hippuric acid by heating the acid with acetic anhydride have been unsuccessful, as also have been experiments on the formation of a cyclic imide by heating hippuramide with *N*-sodium hydroxide or with acetic anhydride. Also, the heating of *r*-acetylalanine and acetic anhydride does not yield a product from which the lactone can be isolated. C. S.

General Reaction for the Conversion of Saturated Fatty Acids, $CH_2R·CH_2·CO_2H$, into Ketones, $R·CO·CH_3$. Henry D. Dakin (*Amer. Chem. J.*, 1910, 44, 41—48).—The generality of the reaction whereby the sodium or ammonium salts of fatty acids are converted into ketones to the extent of 5—10% by excess of 3% hydrogen peroxide (Abstr., 1908, i, 74, 119 ; ii, 720) has been tested. In addition to the cases already recorded, it is found that phenylacetic acid yields benzaldehyde, and phenylbutyric acid a volatile ketone with the odour of benzyl methyl ketone. C. S.

New Method of Alkylation with Benzyl Cyanide. Alkylation of Nitriles of the Formula CHPhR·CN. F. Bodroux and Felix Taboury (*Bull. Soc. chim.*, 1910, [iv], 7, 666—670, 670—672).—An extended account of work already dealt with (this vol., i, 257, 482), fuller details of the method of working being given. The following new data are recorded.

α-Phenyl-β-methylbutyric acid, m. p. 61—62°, obtained by boiling the corresponding nitrile (*loc. cit.*) during thirty-six hours with potassium hydroxide in alcohol, or during six hours if amyl alcohol is used as a solvent, crystallises in colourless prisms.

α-Phenyl-α-ethylbutyramide, m. p. 52°, obtained by hydrolysis of the nitrile (*loc. cit.*), forms colourless prisms, as does also *α-phenyl-γ-methyl-α-propylvaleramide*, $CHMe_2·CH_2·CHPr^{\alpha}Ph·CO·NH_2$, m. p. 84—85°. T. A. H.

1-Acetyl-1-methyl*cyclo*hexane. P. Joseph Tarbouriech (*Compt. rend.*, 1910, 150, 1606—1607. Compare Abstr., 1909, i, 796).—Oxidation of the ketone obtained by the action of acids on *cyclo*hexanolpropan-β-ol leads to the formation of the *ketonic acid*, $C_6H_{10}Me·CO·CO_2H$, b. p. 141°/20 mm. This forms a *semicarbazone*, m. p. 198°, and a *semicarbazone methyl* ester, m. p. 158° ; the *oxime*

decomposes at 160°, losing water and carbon monoxide, and forming the *nitrile*, C_7H_{13}·CN, b. p. 180°, which, on hydrolysis, furnishes an acid identical with Zelinski's 1-methyl*cyclo*hexane-1-carboxylic acid (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 477). The original ketone, therefore, is 1-*acetyl*-1-*methyl*cyclo*hexane*, C_6H_{10}Me·COMe. W. O. W.

α-Amino-*p*-hydroxyphenylacetic Acid. Jules Aloy and Ch. Rabaut (*Bull. Soc. chim.*, 1910, [iv], **7**, 516—518).—The first part of an investigation of the homologues of tyrosine, which are likely to be of biological interest. The preparation and properties of α-amino-*p*-hydroxyphenylacetic acid, the next lower homologue, are described. The acid was prepared by the action of potassium cyanide and ammonium chloride on anisaldehyde, the resulting aminonitrile being hydrolysed and the acid obtained demethylated by Zeisel's method.

α-Amino-p-*methoxyphenylacetonitrile*, OMe·C_6H_4·CH(NH_2)·CN, m. p. 65°, is unstable, and evolves hydrogen cyanide at atmospheric temperatures; the *hydrochloride* is crystalline. The corresponding acid already prepared by Tiemann and Köhler (Abstr., 1882, 57) yields a crystalline hydrochloride, and on demethylation gives *α-amino-p-hydroxyphenylacetic acid*, which crystallises in long, colourless prisms, and yields crystalline *salts* with halogen acids and a pale blue, crystalline *copper* derivative. Chlorine water and bromine water give precipitates; the *bromo*-compound so formed has m. p. 90°. The acid may be characterised by its copper derivative, the red colour produced by Millon's reagent, the blue tint furnished by alkaline hypochlorites, and the fact that tyrosinase produces no change in colour. The last two tests serve to distinguish this acid from tyrosine. T. A. H.

Reduction and Derivatives of *o*-Nitrocinnamoylformic Acid. Gustav Heller (*Ber.*, 1910, **43**, 1923—1927).—[With Edmund Weidner]—*o*-Nitrocinnamoylformic acid forms an *ethyl* ester, m. p. 71°, which separates from alcohol in golden-yellow needles, an *oxime*, m. p. 157°, and *cis*- and *trans*-modifications of the *phenylhydrazide*. The *cis*-form, obtained from the acid and phenylhydrazine in alcohol at 0°, is precipitated from acetone solution by petroleum in tufts of faintly yellow needles, responds to Bülow's hydrazide reaction, easily and smoothly yields indigotin by treatment with alkaline water, and is converted at 100° or by recrystallisation from 50% acetic acid into the *trans*-isomeride, m. p. 222° (decomp.), which is produced directly by treating a hot solution of the acid in 50% acetic acid with phenylhydrazine. The *trans*-modification gives Bülow's reaction, but does not yield indigotin with alkaline water. *o*-Nitrocinnamoylformic acid in ethereal solution is reduced by aqueous ferrous sulphate and ammonium hydroxide to 4-keto-1 : 4-dihydroquinoline-2-carboxylic acid. C. S.

Complete Methylation with Methyl Sulphate. Josef Tambor (*Ber.*, 1910, **43**, 1882—1889).—Waliaschko's extension (Abstr., 1909, i, 248) of Dreker and Kostanecki's generalisation (Abstr., 1893, i, 217) has been supported by the author's experiments, which show that the following fully methylated compounds can be obtained by submitting the partially methylated substances to the repeated energetic action of

methyl sulphate and alkali. 1-Methoxyxanthone from 1-hydroxyxanthone; 2-methoxy-4-ethoxyacetophenone, m. p. 49°, from resacetophenone ethyl ether; 4-methoxy-2-ethoxyacetophenone, m. p. 7°, from resacetophenone methyl ether and ethyl sulphate; resacetophenone dimethyl ether, m. p. 44°, from the monomethyl ether; 2-hydroxy-4-methoxydeoxybenzoin, m. p. 90°, from 2 : 4-dihydroxydeoxybenzoin, and by a repetition of the process, 2 : 4-dimethoxydeoxybenzoin, m. p. 56°.

[With A. Schürch]—*Methyl 2′-hydroxy-4′-methoxy-2-benzoylbenzoate*, $OMe\cdot C_6H_3(OH)\cdot CO\cdot C_6H_4\cdot CO_2Me$, m. p. 103°, and the corresponding acid are both obtained when ethyl resorcinolphthalein is heated for twelve hours with methyl iodide (2 mols.) and alcoholic potassium hydroxide (2 mols.). Ethylation of resorcinolphthalein in a similar manner yields *2′-hydroxy-4′-ethoxy-2-benzoylbenzoic acid*, m. p. 173°, and its ethyl *ester*, m. p. 78°. Reduction of 2′-hydroxy-4′-methoxy-2-benzoylbenzoic acid by zinc dust and alcoholic potassium hydroxide leads to the formation of *2′-hydroxy-4′-methoxy-2-benzylbenzoic acid*, m. p. 140°, a hot alcoholic solution of which with methyl sulphate (3 mols.) and potassium hydroxide (3 mols.) forms the potassium salt of 2′ : 4′-*dimethoxy-2-benzylbenzoic acid*, m. p. 149°; the acid in carbon disulphide is converted by phosphorus pentachloride into the corresponding acid *chloride*, m. p. 166°. Resorcinolphthalein is easily and completely methylated by methyl sulphate (3 mols.) and potassium hydroxide (3 mols.), yielding *methyl* 2′ : 4′-*dimethoxy-2-benzoylbenzoate*, m. p. 100°. 2′ : 4′-Dimethoxy-2-benzoylbenzoic acid is reduced by zinc dust and alkali to the 2 : 4-*dimethoxyphenylphthalide*,

$$C_6H_3(OMe)_2\cdot CH<\begin{matrix}--O--\\ C_6H_4\end{matrix}>CO,$$ m. p. 107°.

β-Resorcylic acid, methyl sulphate, and sodium hydroxide yield, according to the experimental conditions, either *p*-methoxysalicylic acid or β-resorcylic acid dimethyl ether. The chloride of the latter and phloroglucinol trimethyl ether condense in the presence of aluminium chloride to form 2 : 4 : 6 : 2′ : 4′-*pentamethoxybenzophenone*, m. p. 138°, which is reduced by zinc and alcoholic alkali to 2 : 4 : 6 : 2′ : 4′-*pentamethoxybenzhydrol*, m. p. 104°. 2 : 4 : 2′ : 4′-*Tetramethoxybenzophenone* has m. p. 130°. 3 : 4 : 2′ : 4′-*Tetramethoxybenzophenone*, m. p. 124°, separates from concentrated alcoholic solution in yellow, prismatic needles, and from dilute solution in small, white leaflets. 2′ : 4 : 4′-*Trimethoxybenzophenone* has m. p. 73—74°. C. S.

Researches in Benzidine Formation. Henri Duval (*Bull. Soc. chim.*, 1910, [iv], 7, 677—683).—A résumé of information already published, in part, in Abstr., 1905, i, 651; 1909, i, 747. The following new data are given. 2 : 2′-Dinitrodiphenylmethane-4 : 4′-dicarboxylic acid, when purified through the ethyl ester, has m. p. 296°, and dissolves in excess of alkali, forming a violet-coloured solution. On reduction with stannous chloride and hydrochloric acid in alcohol, the ethyl ester yields ethyl 2 : 2′-diaminodiphenylmethane-4 : 4′-dicarboxylate, m. p. 150° (compare Abstr., 1905, i, 651), whilst reduction with zinc dust and ammonium chloride, followed by oxidation by means of a current of air in presence of potassium hydroxide,

furnishes 2 : 2′-azoxydiphenylmethane-4 : 4′-dicarboxylic acid (Abstr., 1909, i, 747). The *ethyl* ester of this acid, m. p. 224°, crystallises in bright yellow needles, and on reduction with zinc dust and acetic acid yields *ethyl* 2 : 2′-*hydrazodiphenylmethane*-4 : 4′-*dicarboxylate*, m. p. 165°, which crystallises in colourless needles, and on oxidation with yellow mercuric oxide gives ethyl 2 : 2′-azodiphenylmethane-4 : 4′-dicarboxylate (*loc. cit.*). T. A. H.

Condensation of Ethyl Oxalate with *o*- and *p*-Xylylene Cyanides. Wilhelm Wislicenus and Otto Penndorf (*Ber.*, 1910, 43, 1837—1842. Compare Hinsberg, this vol., i, 486).—The small yields of xylylene cyanides obtained by the action of an aqueous-alcoholic potassium cyanide solution on the bromides are due to the formation of xylylene diethyl ethers. A theoretical yield of the p-*ether*, $C_{12}H_{18}O_2$, can be obtained by the action of an alcoholic solution of potassium ethoxide on *p*-xylylene bromide. It is a colourless liquid, b. p. 251—252°/734 mm., with a pleasing odour, and when boiled with concentrated hydrochloric acid yields *p*-xylylene chloride.

An 80% yield of *o*-xylylene cyanide can be obtained if suitable precautions are taken. A benzene solution of this cyanide condenses with ethyl oxalate in the presence of sodium ethoxide, yielding Hinsberg's 2 : 3-dihydroxy-1 : 4-dicyanonaphthalene,

$$C_6H_4\begin{<}C(CN):C\cdot OH \\ C(CN):C\cdot OH'\end{<}$$

which crystallises in colourless needles, containing $1H_2O$, m. p. 278—279°; when anhydrous the compound has m. p. 290—291° (decomp.). With only a small amount of ferric chloride, it gives a reddish-violet coloration, but with a larger quantity of the ferric salt a deep blue colour (compare Hinsberg).

p-Xylylene cyanide also condenses with ethyl oxalate, yielding *ethyl* ω*β-dicyano*-p-*tolylpyruvate*, $CN\cdot CH_2\cdot C_6H_4\cdot CH(CN)\cdot CO\cdot CO_2Et$, which crystallises in glistening, colourless, flat needles, m. p. 135—136°. It gives a blackish-green coloration with ferric chloride, and a brown *copper* derivative. When benzoylated in pyridine solution it yields a *benzoyl* derivative, $C_{12}H_{16}O_4N_2$, m. p. 99—101°.

With alcoholic potassium hydroxide it yields potassium oxalate and *p*-xylylene cyanide.

When boiled for ten hours with 25% sulphuric acid it yields p-*phenyleneaceticpyruvic acid*, $CO_2H\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot CO\cdot CO_2H$, m. p. 199—200°.

When the ester is hydrolysed by saturating with hydrogen chloride a solution in ethyl alcohol to which the theoretical amount of water has been added, a product, $C_{14}H_{13}O_5N$, m. p. 180—181°, is obtained. This is either the *imide* of p-*phenyleneacetic-oxalacetic acid*,

$$CO_2Et\cdot CH_2\cdot C_6H_4\cdot CH\begin{<}CO\cdot CO \\ CO\cdot NH'\end{<}$$

or *ethyl hydroxymaleinimide*-p-*phenylacetate*,

$$CO_2Et\cdot CH_2\cdot C_6H_4\cdot C\begin{<}C(OH)\cdot CO \\ CO\text{——}NH\end{<}$$

Its solutions in alkalis have a deep yellow colour, and it yields a red

sodium salt. Ethyl cyanophenylpyruvate, when hydrolysed in a similar manner, yields hydroxyphenylmaleinimide (Volhard and Henke, Abstr., 1895, i, 103). J. J. S.

Action of Light on Benzaldehyde in the Presence of Iodine. Luigi Mascarelli and N. Bosinelli (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 562—563).—The oil of b. p. 189—191°/18 mm., which is one of the products of this reaction, and which was formerly described (this vol., i, 389) as a dimeric form of benzaldehyde, has been further investigated, and has proved to be benzyl benzoate. It has b. p. 315—320°, is but slightly volatile in steam, and is quantitatively saponified when boiled with alcoholic potassium hydroxide.

R. V. S.

2 : 3-Dihydroxybenzaldehyde ; *o*-Protocatechuic Aldehyde. Hermann Pauly and Karl Lockemann (*Ber.*, 1910, **43**, 1813—1814. Compare Nölting, this vol., i, 176).—2 : 3-*Dihydroxybenzaldehyde*, $CHO\cdot C_6H_3(OH)_2$, prepared by heating *o*-vanillin with glacial acetic acid and concentrated aqueous hydrobromic acid, crystallises in sulphur-yellow needles, m. p. 108°, and b. p. 235°. Its solution in water has a green colour, and in alkalis an orange-red colour. Its barium salt with carbonyl chloride yields the cyclic *carbonate*,

$$CHO\cdot C_6H_3<^{O}_{O}>CO,$$

in the form of colourless crystals, m. p. 105°, and when this is boiled with methyl alcohol a *methyl* ester, m. p. 115°, is obtained.

The *phenylhydrazone*, m. p. 176°, and the *semicarbazone*, m. p. 226°, are colourless, whereas the Schiff's bases are intensely coloured, although the corresponding compounds derived from other dihydroxybenzaldehydes are colourless. The *anil* is bright scarlet with a bluish tinge, so also are the derivatives with β-naphthylamine and benzidine. J. J. S.

Transformation of Non-cyclic Diketones into Cyclic Compounds. Edmond É. Blaise and A. Koehler (*Bull. Soc. chim.*, 1910, [iv], **7**, 655—661).—Published already for the most part in Abstr., 1909, i, 287 ; and this vol., i, 463. The following additional facts are given. 2-Acetyl-1-methyl-Δ′-*cyclo*pentene, b. p. 66—68°/9 mm., or 188—189°/755 mm. (compare Perkin and Marshall, Trans., 1890, **57**, 241), yields a *semicarbazone*, m. p. 180°, and on oxidation with permanganate furnishes acetic and γ-acetyl-*n*-butyric acids. γ-Propionyl-*n*-butyric acid yields a *semicarbazone*, m. p. 196°, and a *p-nitrophenylhydrazone*, m. p. 123°, which forms microscopic crystals.

T. A. H.

Condensation of Aldehydes with Methyl Nonyl Ketone, α-Naphthyl Methyl Ketone and *p*-Methoxyacetophenone, and the Formation of Pyridine Derivatives from the Condensation Products. Max. Scholtz and W. Meyer (*Ber.*, 1910, **43**, 1861—1866. Compare Abstr., 1895, i, 563 ; 1899, i, 717 ; 1903, i, 436).—α-Benzylidenemethyl nonyl ketone [styryl nonyl ketone], $CHPh{:}CH\cdot CO\cdot C_9H_{19}$, has been prepared by Carette (Abstr., 1901, i, 13).

The *semicarbazone*, $C_{19}H_{29}ON_3$, crystallises in yellow needles, m. p. 121°. The isomeric γ-benzylidene derivative, obtained by condensing benzaldehyde with methyl nonyl ketone in the presence of hydrogen chloride (Goldschmidt and Krczmar, Abstr., 1902, i, 40; Harries and Müller, *ibid.*, 1902, i, 295), forms a *hydrochloride*, $C_{18}H_{27}OCl$, which crystallises in snow-white needles, m. p. 77°. The *ketone*, $CH_3{\cdot}CO{\cdot}C(:CHPh){\cdot}C_8H_{17}$, is an oil, and yields a *semicarbazone*, $C_{19}H_{29}ON_3$, in the form of glistening plates, m. p. 130°.

α-Cinnamylidenemethyl nonyl ketone, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}C_9H_{19}$, crystallises in glistening, yellow plates, m. p. 83°. The *semicarbazone*, $C_{21}H_{31}ON_3$, forms pale yellow needles, m. p. 154°, and the *oxime*, $C_{20}H_{29}ON$, yellow, felted needles, m. p. 89°. When distilled, the oxime yields 6-*phenyl*-2-*nonylpyridine*, $C_{20}H_{27}N$, which is a pale yellow oil, b. p. 165—170°/30 mm.; the *platinichloride* $(C_{20}H_{27}N)_2,H_2PtCl_6$, crystallises in pale red needles, m. p. 201°.

α-Piperonylidenemethyl nonyl ketone, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C_9H_{19}$, crystallises in pale yellow, felted needles, m. p. 56°; *semicarbazone*, $C_{20}H_{29}O_3N_3$, forms colourless needles, m. p. 151°. p-*Methylstyryl nonyl ketone*, $C_6H_4Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C_9H_{19}$, crystallises in plates, m. p. 129°. p-*Methoxystyryl nonyl ketone*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_9H_{19}$, forms colourless, glistening plates, m. p. 63°, and yields a *semicarbazone*, $C_{20}H_{31}O_2N_3$, in the form of pale yellow needles, m. p. 114°. p-iso-*Propylstyryl nonyl ketone*, $C_3H_7{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_9H_{19}$, forms soft, colourless needles, m. p. 144°.

The *semicarbazone* of α-naphthyl methyl ketone, $C_{13}H_{13}ON_3$, forms colourless crystals, m. p. 205°. *Cinnamylidenemethyl α-naphthyl ketone*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}C_{10}H_7$, is an oil; the *oxime*, $C_{21}H_{17}ON$, crystallises in yellow needles, m. p. 123°, and, when distilled, yields a small amount of 6-*phenyl*-2-*α-naphthylpyridine*, $C_{21}H_{15}N$, as a pale yellow oil, b. p. 190—192°/12 mm., but the *platinichloride* of which crystallises in pale red needles, m. p. 109°.

p-*Nitrostyryl α-naphthyl ketone*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_{10}H_7$, forms yellow needles, m. p. 131°.

The *semicarbazone* of *p*-acetylanisole, $C_{10}H_{10}O_2N_3$, forms colourless plates, m. p. 198°. *Cinnamylidenemethyl* p-*methoxyphenyl ketone*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

crystallises in yellow, felted needles, m. p. 93°; its *semicarbazone*, $C_{19}H_{18}O_2N_3$, has m. p. 189°, and its *oxime*, $C_{18}H_{17}O_2N$, forms yellow needles, m. p. 147°, and, when distilled, yields 2-*phenyl*-6-*anisylpyridine*, $C_{18}H_{15}ON$, as pale yellow needles, m. p. 119°.

Piperonylidene-p-*methoxyacetophenone*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

forms pale yellow, glistening needles, m. p. 129°, and *cinnamylidenemethyl benzyl ketone*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2Ph$, similar needles, m. p. 119°. J. J. S.

The Friedel-Crafts' Reaction with Chlorides of Unsaturated Acids. Elmer P. Kohler, Gertrude L. Heritage, and M. C. Burnley (*Amer. Chem. J.*, 1910, **44**, 60—76. Compare Abstr., 1907, i, 1050; 1909, i, 938).—Cinnamoyl chloride and excess of benzene in carbon disulphide react with aluminium chloride to form ββ-diphenyl-

propiophenone, 3-keto-1-phenyl-2 : 3-dihydroindene, and β-chloro-β-phenylpropiophenone; styryl phenyl ketone cannot be isolated. Under similar conditions, cinnamoyl chloride reacts with bromobenzene to form about 25% of p-*bromophenyl styryl ketone*, $CHPh{:}CH{\cdot}CO{\cdot}C_6H_4Br$, m. p. 100—101°, and 6-*bromo*-3-*keto*-1-*phenyl*-2 : 3-*dihydroindene*, $C_6H_3Br\langle^{CHPh}_{CO}\rangle CH_2$, m. p. 60—61°, in 30—35% yield. With anisole or phenetole, cinnamoyl chloride yields only the expected unsaturated ketones.

αβ-Dibromo-β-phenylpropionyl chloride is conveniently prepared by adding phosphorus pentachloride to a suspension of dibromocinnamic acid in phosphoryl chloride, removing the chlorides of phosphorus at 150—160° under diminished pressure, and crystallising the residue from carbon disulphide and petroleum. In carbon disulphide cooled by a freezing mixture, the chloride reacts with aluminium chloride alone, hydrogen bromide and a little chloride being evolved, and phenylacetylene, bromostyrene, *p*-bromocinnamic acid, cinnamic acid, α-bromocinnamic acid, and a small quantity of other unidentified products being formed.

αβ-Dibromo-β-phenylpropionyl chloride, benzene, and aluminium chloride react in carbon disulphide at −20° to form a substance, m. p. 89—90°, which is not dibromophenylpropiophenone, as stated by Collet, but 2-bromo-3-keto-1-phenyl-2 : 3-dihydroindene, the *semicarbazone* of which has m. p. 212° (decomp.). With bromobenzene, dibromophenylpropionyl chloride yields, in addition to a large quantity of acid by-products due to the reaction between the acid chloride and the aluminium chloride, 2 : 6-*dibromo*-3-*keto*-1-*phenyl*-2 : 3-*dihydroindene*, m. p. 143—144°, and an isomeric substance, m. p. 86°, which is probably a stereoisomeride, since both substances yield p-*bromo*-o-*benzoylbenzoic acid*, m. p. 174°, by oxidation by potassium permanganate in acetone, and the substance of higher m. p. is converted almost quantitatively into the other at its m. p. C. S.

Acetylenic Ketones. Émile André (*Compt. rend.*, 1910, **151**, 75—78).—In the preparation of acetylenic ketones from the sodium derivatives of unsaturated hydrocarbons, better yields are obtained by using an acid bromide instead of the acid chloride. iso*Valerylphenylacetylene*, $CPh{:}C{\cdot}CO{\cdot}CH_2Pr^{\beta}$, has b. p. 149—151°/12 mm., D^{20} 0·969, n_D^{20} 1·5405. *Hexoylphenylacetylene*, $C_5H_{11}{\cdot}CO{\cdot}C{:}CPh$, m. p. 14—15°, b. p. 170—172°/12 mm., D^{20} 0·965, n_D^{20} 1·5352, was prepared from *hexoyl bromide*, b. p. 175—176°. The ketones have also been prepared by oxidising the corresponding secondary alcohols (Moureu, Abstr., 1902, i, 289) with chromic acid in acetic acid solution (compare Dupont, this vol., i, 456). The molecular refractions for five ketonic derivatives of phenylacetylene have been determined, and found to exceed the calculated values by about three units. W. O. W.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. VI. Ketochlorides of Dianisylideneacetone [Di-*p*-methoxystyryl Ketone] and Dicinnamylideneacetone. Fritz Straus [with Georg Lutz and Werner Hüssy] (*Annalen*, 1910, **374**, 40—90. Compare this vol., i, 119).—In the main, an amplifica-

tion and extension of the investigations of Straus and Ecker (compare Abstr., 1906, i, 859). Di-*p*-methoxystyryl ketone forms *additive* compounds with the following substances: mercuric chloride, deep yellow, slender, soft needles; calcium chloride, bright yellow powder; phosphoryl chloride, dark reddish-brown oil. The ketone, when treated with phosphorus pentachloride in carbon disulphide, yields the *additive* product, $(OMe\cdot C_6H_4\cdot CH{:}CH)_2CCl_2,PCl_5$, a green, crystalline powder, an ethereal solution of which when treated with ice-water and subsequently with sodium hydrogen carbonate and light petroleum yields the *hydrochloride* of $\beta\beta$-dichloro-$\alpha\gamma$-dianisylidenepropane,

$$(OMe\cdot C_6H_4\cdot CH{:}CH)_2CCl_2,HCl,$$

a dark green powder with a metallic reflex; the ketochloride is obtained from the hydrochloride by boiling with dry petroleum ether, and crystallises in faintly yellow, silvery leaflets, m. p. 91—92° (compare Staudinger, Abstr., 1909, i, 906). $\beta\beta$-Dichloro-$\alpha\gamma$-dianisylidenepropane is converted by water into the *chlorocarbinol*,

$$(OMe\cdot C_6H_4\cdot CH{:}CH)_2CCl\cdot OH(?),$$

an unstable oil. *Additive* compounds of the ketochloride with the following substances have been prepared: mercuric chloride,

$$C_{19}H_{18}O_2Cl_2,4HgCl_2,$$

violet crystals with a green reflex; thionyl chloride,

$$C_{19}H_{18}O_2Cl_2,SOCl_2,$$

green powder; phosphoryl chloride, intensely green oil; carbonyl chloride, unstable, green powder; sulphur dioxide, $3C_{19}H_{18}O_2Cl_2,2SO_2$, a stable, green, crystalline powder; acetonitrile, propionitrile, benzonitrile, and benzyl cyanide, substances soluble in excess to pale blue solutions. The *sulphate*,

$$(OMe\cdot C_6H_4\cdot CH{:}CH)_2CCl\cdot OSO_3H,aH_2SO_4,$$

prepared by adding sulphuric acid to a solution of the ketochloride in methyl sulphate, crystallises in glistening, green leaflets, The ketochloride is converted by chlorine into the dichloride, m. p. 107—108° (compare Straus and Ecker, *loc. cit.*), which is slowly attacked by a solution of chlorine in tetrachloromethane, but apparently not by bromine in chloroform. The ketochloride or its dichloride, when acted on by methyl alcohol, yields the *methyl ether*,

$$(OMe\cdot C_6H_4\cdot CH{:}CH)_2CCl\cdot OMe,$$

of the corresponding chloro-carbinol, which crystallises in tufts of white needles or leaflets, m. p. 87—88°, and dissolves in concentrated sulphuric acid or liquid sulphur dioxide, forming blue solutions. Hydrogen chloride converts the methyl ether, dissolved in light petroleum, into the hydrochloride of the corresponding ketochloride, but when the solvent is benzene or carbon disulphide, the ether is converted into the hydrochloride of the corresponding ketone. The action of methyl alcohol on the ketochloride dichloride leads to the formation of two *methyl ethers* having the composition $C_{20}H_{21}O_3Cl_3$, which are probably cis- and trans-isomerides; the one crystallises in slender, white leaflets, m. p. 99—100°, whilst the other forms colourless needles, m. p. 80—81°; both isomerides are decomposed slowly by methyl alcohol with the elimination of chlorine, and when acted on by active aluminium in an alcoholic solution of sodium methoxide yield the methyl ether of 4:4′-dimethoxydicinnamenyl-

chlorocarbinol. The ketochloride dichloride, when treated with silver oxide, yields the *dichloride* of the chlorocarbinol,

$$OMe\cdot C_6H_4\cdot CHCl\cdot CHCl\cdot CCl(OH)\cdot CH{:}CH\cdot C_6H_4\cdot OMe,$$

which crystallises in felted, slender, white needles, m. p. 121°.

Dicinnamylideneacetone, when acted on by phosphorus pentachloride under suitable conditions, yields the corresponding *ketochloride*, $(CHPh{:}CH\cdot CH{:}CH)_2CCl_2$, which forms colourless crystals, m. p. 114·5°, and when treated with chlorine in tetrachloromethane yields the *tetrachloride*,

$$CHPh{:}CH\cdot CH{:}CH\cdot CCl_2\cdot CHCl\cdot CHCl\cdot CHCl\cdot CHPhCl,$$

which is also obtained by boiling the ketone dissolved in a mixture of benzene and chloroform with phosphorus pentachloride, and forms colourless, compact crystals, m. p. 172° (decomp.). The tetrachloride combines with further quantities of chlorine, forming mixtures of *hexa-* and *octa*-chlorides. The ketochloride also combines with bromine, yielding a *hexabromide*, $C_{21}H_{18}Cl_2Br_6$, which crystallises in tufts of small, colourless prisms decomposing at 219°. The ketochloride forms *additive* products with the following substances: mercuric chloride, $C_{21}H_{18}Cl_2,2HgCl_2$, metallic, green powder; phosphorus pentachloride, $C_{21}H_{18}Cl_2,PCl_5,C_6H_6$, glistening, green, slender leaflets; phosphoryl chloride, glistening, green leaflets; stannic chloride, dark green powder with a green reflex; acetyl chloride, thionyl chloride, and liquid sulphur dioxide, products forming green solutions. The ketochloride also forms green *salts* with sulphuric acid, nitric acid, and hydrogen chloride. The following derivatives of the ketochloride are prepared by methods similar to those already described: *chlorocarbinol*, $C_{20}H_{18}{:}CCl\cdot OH$, long, white needles, m. p. 122°; *methyl ether*, $C_{20}H_{18}{:}CCl\cdot OMe$, slender, white needles or glistening leaflets, m. p. 120·5°. W. H. G.

Dibenzylideneacetone (Distyryl Ketone) and Triphenylmethane. VII. Nature of the Linking of the Halogen Atoms in the Ketohalides of Unsaturated Ketones. II. Fritz Straus [and, in part, with Jean B. Krier and Georg Lutz] (*Annalen*, 1910, 374, 121—198. Compare this vol., i, 119 and preceding abstract; Straus and Ecker, Abstr., 1906, i, 859; Strauss and Caspari, 1907, i, 609; Straus and Ackermann, 1909, i, 489; Straus and Hüssy, *ibid.*, 490).—The ketohalides of *pp*-dimethoxybenzylideneacetophenone have been investigated. They resemble the halides already described, but are more reactive, owing to the presence of the methoxy-substituents. They also yield intensely coloured perbromides and periodides, analogous to those derived from the triphenylmethyl halides. Unlike most of the examples studied previously, it is found that the bromide has a lower m. p. than the chloride.

The chlorobromides have been prepared by the following methods:

$$(1)\ R_1R_2CBrBr \longrightarrow R_1R_2CBr\cdot OH \longrightarrow R_1R_2CBrCl$$
$$(2)\ R_1R_2CClCl \longrightarrow R_1R_2CCl\cdot OH \longrightarrow R_1R_2CClBr,$$

and the products obtained have been found to be identical. This has been proved by determining the amounts of halogen hydracids liberated

by the action of hydroxylic reagents, such as water and methyl alcohol, on the products. The amount of hydrogen bromide formed is much greater than the amount of hydrogen chloride (20%).

It is pointed out that the relative amounts of the two halogen hydracids vary with the constitution of the ketone from which the ketohalides are derived, and thus each case is characterised by a specific equilibrium of the two valency forms.

Water and methyl alcohol transform the ketodichlorides into the corresponding chlorocarbinol and its methyl ether, but these are spontaneously decomposed into the ketone, probably owing to the intermediate formation of an oxonium derivative: $R_1R_2CCl\cdot OMe \longrightarrow R_1R_2C{:}O{<}^{Cl}_{Me} \longrightarrow R_1R_2C{:}O$.

It is found that the keto-dichloride and -dibromide affect one another in solution. When freshly mixed, the solution yields molecular proportions of hydrochloric and hydrobromic acids, but the amount of hydrobromic acid increases at the expense of the hydrochloric, until an equilibrium is established, which is identical with that obtained when a solution of the ketochlorobromide has been kept for some time. The conclusion is drawn that the chlorobromide in solution decomposes to a slight extent into molecular quantities of dichloride and dibromide, and that the three halogen derivatives are present in solution in a state of equilibrium:

$$R_1R_2CCl_2 + R_1R_2CBr_2 \rightleftarrows 2R_1R_2CClBr.$$

When evaporated the solution yields a product with all the properties of the chlorobromide, and this is its simplest method of formation; after purification, a solution of the product gives the usual relative amounts of hydrochloric and hydrobromic acids, but in the course of time returns to the above-mentioned equilibrium. Coloured intermediate products are not formed, and all the reactions are attributed to decompositions into colourless ions (compare Hantzsch and Meyer, this vol., i, 238): $2CR_1R_2ClBr \rightleftarrows CR_1R_2Cl^{\cdot} + CR_1R_2Br^{\cdot} + Cl' + Br' \rightleftarrows CR_1R_2Cl_2 + CR_1R_2Br_2$.

The solid chlorobromide is regarded as the pure compound, CR_1R_2ClBr, and dissociation is supposed to take place on fusion or solution.

The formation of the ketodibromide from the chlorobromide and bromine or hydrogen-bromide is not merely due to the relative amounts of the valency isomerides present, but also depends on the rapidity with which the equilibrium between the ketohalides is attained, and this varies with different ketones.

Di-p-methoxyphenyl styryl ketone, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot C_6H_4\cdot OMe$ obtained by condensing acetylanisole (Abstr., 1890, 963) with anisaldehyde in the presence of sodium ethoxide (5% solution), crystallises in yellow prisms, m. p. 101—102°, and gives a reddish-yellow coloration with concentrated sulphuric acid. The *compound* with mercuric chloride, $C_{17}H_{16}O_3,HgCl_2$, forms golden-yellow needles, m. p. 150°, and is much more stable than the corresponding derivative of distyryl ketone. The *dibromide*, $OMe\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot CO\cdot C_6H_4\cdot OMe$, forms snow-white crystals, m. p. 140° (decomp.), and when boiled with ten times its weight of methyl alcohol for twenty minutes yields the

methyl ether, $OMe\cdot C_6H_4\cdot CH(OMe)\cdot CHBr\cdot CO\cdot C_6H_4\cdot OMe$, as colourless needles, m. p. 108—109°, which dissolve in concentrated sulphuric acid to cherry-red solutions.

The *ketodichloride*, p-*methoxyphenyl*-p-*methoxystyryldichloromethane*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CCl_2\cdot C_6H_4\cdot OMe$, is best isolated as its additive *compound* with phosphorus pentachloride, $C_{17}H_{16}O_2Cl_2,PCl_5$, which forms steel-blue crystals. The ketodichloride crystallises from a mixture of carbon disulphide and light petroleum in brilliant colourless, compact prisms, melting at 78° to a green liquid. The *compound*, $C_{17}H_{16}O_2Cl_2,4HgCl_2$, forms brownish-violet needles, and is most useful for characterising the chloride. The *hydrochloride*, $C_{17}H_{16}O_2Cl_2,HCl$, forms slender, blue needles, and the *periodide*, $C_{17}H_{16}O_2Cl_2I_4$, dark crystals, m. p. 81—83°, which are partially decomposed by most solvents. The *sulphate* has not been obtained crystalline, and an additive compound with carbon disulphide has not been isolated. The ketochloride reacts with a carbon tetrachloride solution of chlorine, yielding the *additive* compound,

$$OMe\cdot C_6H_4\cdot CHCl\cdot CHCl\cdot CCl_2\cdot C_6H_4\cdot OMe,$$

in the form of an unstable oil, which appears to be identical with the product obtained by the action of an excess of phosphorus pentachloride on a benzene solution of the ketone. A solution of bromine in carbon disulphide yields the *perbromide*, $C_{17}H_{16}O_2ClBr,Br_2$, in the form of a green precipitate, m. p. 120° (decomp.).

Thionyl chloride and phosphoryl chloride yield precipitates, but phosphorus trichloride, acetyl chloride, and nitriles do not. Nitriles yield pale blue solutions, and liquid sulphur dioxide an intense violet solution.

p-Chlorophenyl-*p*-chlorostyryldichloromethane (Abstr., 1909, i, 489) yields a *dichloride*, *αγ-di*-p-*chlorophenyl-aaβγ-tetrachloropropane*,

$$C_6H_4Cl\cdot CHCl\cdot CHCl\cdot CCl_2\cdot C_6H_4Cl,$$

which crystallises from methyl alcohol in slender, colourless needles, m. p. 101°. The compound is formed slowly, and when reduced with active aluminium and sodium methoxide dissolved in methyl alcohol yields 4 : 4′-*dichlorophenylbenzylacetylene*, $C_6H_4Cl\cdot C{:}C\cdot CH_2\cdot C_6H_4Cl$, as colourless plates, m. p. 80—80·5°.

p-Methoxyphenyl-*p*-methoxystyryldichloromethane reacts readily with water, and also with methyl alcohol, yielding 4 : 4′-*dimethoxyphenylstyrylchlorocarbinol*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CCl(OH)\cdot C_6H_4\cdot OMe$, and its *methyl ether*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CCl(OMe)\cdot C_6H_4\cdot OMe$. The carbinol crystallises as colourless, felted needles, m. p. 75—76°, and the methyl ether as glistening, colourless plates, m. p. 44—45°. Both compounds are extremely unstable, and in their preparation it is necessary to avoid light and all traces of acid. The carbinol reacts readily with concentrated hydrochloric acid, regenerating the ketodichloride, and the methyl ether with glacial acetic acid yields the ketone.

The *ketodibromide*, 4 : 4′-*dimethoxyphenylstyryldibromomethane*, cannot be prepared by the action of phosphorus pentabromide on the ketone or its hydrobromide, but can be obtained by the action of phosphorus tribromide on a benzene solution of the ketone. The reaction is slow, and is of use only with ketones containing a reactive carbonyl group, especially those containing methoxy-substituents. The ketobromide is

best isolated as its complex with mercuric bromide, or, in certain cases, as its additive compound with bromine, and can be obtained from the mercuric bromide compound by conversion into the bromocarbinol and treatment with hydrobromic acid.

4 : 4′-*Dimethoxyphenylstyrylbromocarbinol*,

$$OMe\cdot C_6H_4\cdot CH{:}CH\cdot CBr(OH)\cdot C_6H_4\cdot Me,$$

crystallises in long, colourless, felted needles, m. p. 83—84°, is only moderately stable, and is immediately decomposed by mineral acids, regenerating the ketone; with hydrobromic acid it yields 4 : 4′-*dimethoxyphenylstyryldibromomethane*,

$$OMe\cdot C_6H_4\cdot CH{:}CH\cdot CBr_2\cdot C_6H_4\cdot OMe,$$

which can be crystallised with some difficulty from a mixture of carbon disulphide and light petroleum. It forms long, lemon-yellow prisms, m. p. 64°, to a green liquid, and gives rises to the following derivatives: $C_{17}H_{16}O_2Br_2,3HgBr_2$, small, violet needles; *perbromide*, $C_{17}H_{16}O_2Br_2,Br_2$, green crystals, m. p. 128—130°, can be obtained by the action of either bromine or phosphorus pentabromide on the ketodibromide; *periodide*, $C_{17}H_{16}O_2Br_2,I_2$, green crystals, m. p. 104—106° (decomp.); *hydrobromide*, $C_{17}H_{16}O_2Br_2,HBr$, steel-blue needles, m. p. 90—95°; *sulphate*, green, glistening needles; *nitrate*, steel-blue, sparingly soluble needles; $C_{17}H_{16}O_2Br_2,SO_2$, bluish-green, glistening crystals. The ketodibromide also yields bluish-green, crystalline precipitates with solutions of zinc chloride, ferric chloride, and mercuric chloride in concentrated hydrochloric acid. Water or silver oxide and ether transform the ketodibromide into the bromocarbinol, glacial acetic acid transforms it into the ketone, and methyl alcohol transforms first into the methyl ether of the bromocarbinol (one to two minutes) and ultimately (eight hours) into the ketone. The *methyl ether*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CBr(OMe)\cdot C_6H_4\cdot OMe$, crystallises in colourless, glistening plates, m. p. 39·5—40·5°.

Phosphorus tribromide reacts with a boiling ethereal solution of di-*p*-methoxystyryl ketone, giving a quantitative yield of the *hydrobromide* of the ketone, $C_{19}H_{18}O_3,HBr$, as a dark reddish-violet precipitate. Phosphorus tribromide, when boiled with a benzene solution of di-*p*-methoxystyryl ketone, yields *di*-p-*methoxystyryldibromomethane*, which can be isolated as its green complex with mercuric bromide. When this complex is shaken with a solution of potassium bromide in 66% methyl alcohol, *di*-p-*methoxystyrylbromocarbinyl methyl ether*, $(OMe\cdot C_6H_4\cdot CH{:}CH)_2CBr\cdot OMe$, is formed. It crystallises in snow-white plates, m. p. 102—103°, and its solution in concentrated sulphuric acid has a pure blue colour.

Phosphorus pentabromide reacts with a carbon disulphide solution of distyryl ketone or its hydrobromide, yielding the same products as does bromine itself (compare Vörlander and Siebert, Abstr., 1904, i, 900). With phosphorus tribromide, the ketodibromide is formed, and this can be isolated as the *tetrabromo*-compound,

$$CHBrPh\cdot CHBr\cdot CBr_2\cdot CH{:}CHPh,$$

m. p. 170° (decomp.).

Di p-*methoxyphenylstyrylchlorobromomethane*,

$$OMe\cdot C_6H_4\cdot CH{:}CH\cdot CBrCl\cdot C_6H_4\cdot OMe,$$

is more readily obtained by the action of hydrochloric acid on the

bromocarbinol than by that of hydrobromic acid on the chlorocarbinol, as the latter reaction is accompanied by side reactions. It crystallises in brilliant, lemon-yellow prisms, m. p. 71°, to a green liquid. Its addition to the ketodibromide raises the m. p. The *complex*, $C_{17}H_{16}O_2ClBr,2HgBr_2$, forms reddish-violet needles; the *perbromide*, $C_{17}H_{16}O_2ClBr,Br_2$, has m. p. 122° (decomp.); the *periodide* forms a brilliant green, crystalline precipitate, m. p. 102—104° (decomp), and the *hydrobromide*, steel-blue needles, and in its preparation a portion of the chlorine becomes replaced by bromine. The additive compound with sulphur dioxide forms green, metallic, glistening crystals, which are unstable. The ketodibromide and the chlorobromide are not affected when shaken with dry benzene and silver chloride. J. J. S.

Terpenes and Ethereal Oils. CII. Otto Wallach (*Annalen*, 1910, 374, 217—235).—I. *Preparation of Hydroxy-ketones and* 1 : 2-*Glycols from the Nitrosochlorides of Semicyclic Hydrocarbons.*—Both of the nitrosochlorides derived from 1-methyl-4-ethylidene*cyclo*hexane react with a mixture of anhydrous sodium acetate and glacial acetic acid at 63—70°, yielding the *oxime* of 4-*acetoxy*-1-*methyl*cyclo*hexyl methyl ketone*, $CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C(OAc)\cdot CMe{:}N\cdot OH$, m. p. 111—112°, together with the oxime of *p*-acetylmethyl*cyclo*hexene; the latter compound is also formed when the oxime melting at 111—112° is distilled.

When the oxime is hydrolysed with 5% sulphuric acid, 4-*hydroxy*-4-*acetylhexahydrotoluene* (4-*hydroxy*-1-*methyl*cyclo*hexyl methyl ketone*), $CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>CAc\cdot OH$, is formed. It has b. p. 223—224° and m. p. 21—22°, and is only sparingly volatile in steam; its *semicarbazone* crystallises in plates, m. p. 219—220°, and its *oxime* has m. p. 128°. When boiled with 20% sulphuric acid, the hydroxy-ketone yields *p*-acetylmethyl*cyclo*hexene, and when treated with magnesium methyl iodide yields *menthan*-4 : 8-*diol* (4 : 8-*terpin*),

$$CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C(OH)\cdot CMe_2\cdot OH,$$

which exists in two stereoisomeric forms, melting respectively at 97—98° and 82—83°. The less fusible compound has b. p. 245°, and yields a liquid bromide; when oxidised, it yields *p*-methyl*cyclo*hexanone. The glycol, m. p. 82—83°, is more readily soluble than its isomeride, and both compounds are readily volatile in steam.

II. *The Terpinene Question* (compare Wallach, Abstr., 1907, i, 1058; 1908, i, 813; Auwers and Heyden, Abstr., 1909, i, 593; Müller, Walbaum, and Müller, *Schimmel's Ber.*, 1909, ii, 16, 33).—A brief summary of researches on terpinenes. It is pointed out that all terpinenes, even that obtained from terpinene dihydrochloride, contain both $\Delta^{1:3}$-dihydro-*p*-cymene and the isomeric $\Delta^{1:4}$-compound. The presence of the former has been established by its conversion into $\alpha\delta$-dihydroxy-α-methyl-δ'-*iso*propyladipic acid, and it is this constituent of the terpinene which yields the nitrosite, m. p. 155°. The presence of $\Delta^{1:4}$-dihydro-*p*-cymene has been proved by its oxidation to the

erythritol (1 : 2 : 3 : 4-tetrahydroxyterpane), which can be transformed by loss of water into a mixture of carvacrol and thymol (Gildmeister and Müller, *Schimmel's Ber.*, 1909, ii, 16). α-Terpinene = $\Delta^{1:3}$-dihydro-*p*-cymene = $\Delta^{1:3}$-menthadiene = carvenene (Semmler). β-Terpinene = $\Delta^{1(7):4}$-menthadiene; γ-terpinene = $\Delta^{1:4}$-dihydro-*p*-cymene = $\Delta^{1:4}$-menthadiene = *iso*carvenene (Semmler). So far, neither $\Delta^{1:3}$- nor $\Delta^{1:4}$-menthadiene has been obtained free from its isomeride, and the same appears to hold good for all doubly-unsaturated cyclic hydrocarbons.

J. J. S.

pp-Dibromobenzil. Heinrich Biltz, H. Edlefsen, and Karl Seydel (*Ber.*, 1910, 43, 1815—1820. Compare Biltz, Abstr., 1908, i, 575; 1909, i, 839).—Di-*p*-bromobenzil yields a *monoxime*, $C_{14}H_9O_2NBr_2$, in the form of minute, colourless needles, m. p. 159—160°, and a *phenylhydrazone*, $C_{20}H_{14}ON_2Br_2$, m. p. 189°. It does not yield a semicarbazone, but forms 3-*oxy*-5 : 6-*di*-p-*bromophenyl*-2 : 1 : 4-*triazine*, $C_6H_4Br\cdot C\!:\!N\cdot CO$ / $C_6H_4Br\cdot C\!:\!N\cdot NH$, when heated with semicarbazide hydrochloride and dilute acetic acid. This crystallises in colourless needles, m. p. 253°, and yields a *sodium* derivative, $C_{15}H_8ON_3Br_2Na$, in the form of pale yellow prisms, and an *acetyl* derivative, $C_{17}H_{11}O_2N_3Br_2$, in the form of hexagonal, colourless plates, m. p. 282°, which are readily hydrolysed.

Di-p-*bromobenzilic acid*, $OH\cdot C(C_6H_4Br)_2\cdot CO_2H$, prepared by the action of an alcoholic solution of sodium ethoxide on the dibromobenzil at the ordinary temperature, crystallises from a mixture of chloroform and light petroleum in needles, m. p. 108—110°, and when heated with carbamide at 220° yields 5 : 5-dibromophenylhydantoin. When heated for three to four hours at 180°, the acid loses carbon dioxide and yields *di*-p-*bromobenzhydrol*, $OH\cdot CH(C_6H_4Br)_2$, which crystallises in glistening, colourless plates, m. p. 174—175°.

Di-p-*bromodiphenylacetic acid*, $CH(C_6H_4Br)_2\cdot CO_2H$, obtained by reducing the benzilic acid with hydriodic acid and red phosphorus in the presence of acetic acid, crystallises in needles, m. p. 187—188°.

Dibromodeoxybenzoin, $C_6H_4Br\cdot CO\cdot CH_2\cdot C_6H_4Br$, obtained by reducing dibromobenzil with zinc dust and glacial acetic acid, crystallises in long, brittle needles, m. p. 141—142°, and does not yield an oxime, a phenylhydrazone, or a semicarbazone. J. J. S.

Acylated Aminoanthraquinones and Anthraquinone Mercaptans and their Behaviour on Vegetable Fibres. Chr. Seer and R. Weitzenböck (*Monatsh.*, 1910, 31, 371—377).—Recently vat-dyes of the anthraquinone series have been obtained by the action of benzoyl chloride on aminoanthraquinones dissolved in nitrobenzene (*Chem. Zeit.*, 1909, No. 108). The authors have now prepared acylated aminoanthraquinones in a similar manner, and find that they are pronounced vat-dyes, giving on unmordanted cotton tones which are deeper than those of the analogous benzoylated compounds. The *anide*, $C_6H_4<^{CO}_{CO}>C_6H_3\cdot NH\cdot CO\cdot C_6H_3<^{CO}_{CO}>C_6H_4$, m. p. 350°, ob-

tained by heating 2-aminoanthraquinone and the chloride of anthraquinone-2-carboxylic acid in nitrobenzene for half an hour, forms pale yellow crystals, and in the hyposulphite vat produces feeble yellow tones on unmordanted cotton. The *amides*, obtained from the same acid chloride and 1 : 5-, 1 : 3-, and 1 : 8-diaminoanthraquinones respectively, produce on unmordanted cotton in the hyposulphite vat brown to brownish shades, which are changed to brown to brick-red by atmospheric oxidation. The *amide*, $C_{28}H_{15}O_6NS$, m. p. 257°, obtained from 1-aminoanthraquinone and anthraquinone-2-sulphonyl chloride, yields a dark red vat, which produces brown shades changing to faint greyish-green by oxidation. 1 : 5-Diaminoanthraquinone and anthraquinone-2-sulphonyl chloride yield the *amide*,

$$C_{14}H_6O_2(NH\cdot SO_2\cdot C_6H_3<^{CO}_{CO}>C_6H_4)_2,$$

m. p. 391°, the vat of which is dark red, producing faint red shades changing to light yellow by oxidation.

1 : 5-Diaminoanthraquinone and picryl chloride in nitrobenzene yield *dipicryl*-1 : 5-*diaminoanthraquinone*,

$$C_6H_2(NO_2)_3\cdot NH\cdot C_6H_3<^{CO}_{CO}>C_6H_3\cdot NH\cdot C_6H_2(NO_2)_3,$$

which decomposes above 340°, and forms a brown vat in alkaline hyposulphite, which produces dark green shades on unmordanted cotton ; these shades are changed by oxidation to violet, which are turned brown by the addition of dilute hydrochloric acid.

Anthraquinone-1-thiol and benzoyl chloride in nitrobenzene yield *benzoylanthraquinone*-1-*thiol*, $C_6H_4<^{CO}_{CO}>C_6H_3\cdot SBz$, m. p. 208°, which forms yellow crystals, and has not the slightest affinity for vegetable fibres. C. S.

Action of Benzyl Chloride and of Monochloroacetic Acid on Aminoanthraquinones. Chr. Seer and R. Weitzenböck (*Monatsh.*, 1910, **31**, 379—386).—In view of the fact that the introduction of acyl groups into the amino-groups of aminoanthraquinones converts these coloured but non-dyeing substances into strong dyes, the effect of the introduction of benzyl, *p*-chlorobenzyl, and glycine-groups has been examined. The products do not possess the character of vat-dyes.

1-*Benzylaminoanthraquinone*, m. p. 189°, obtained from 1-aminoanthraquinone and benzyl chloride at 170—175°, forms red needles, and is reduced by alkaline hyposulphite to the corresponding dihydroanthraquinone. 1-*Anthraquinonylglycine*,

$$C_6H_4<^{CO}_{CO}>C_6H_3\cdot NH\cdot CH_2\cdot CO_2H,$$

m. p. 218—226° (decomp.), obtained from 1-aminoanthraquinone, anhydrous sodium acetate, and chloroacetic acid at 170°, is a brick-red powder. 1 : 5-*Diglycinoanthraquinone*,

$$CO_2H\cdot CH_2\cdot NH\cdot C_6H_3<^{CO}_{CO}>C_6H_3\cdot NH\cdot CH_2\cdot CO_2H,$$

obtained from 1 : 5-diaminoanthraquinone in a similar manner, is a dark red powder, which dyes wool directly, and dissolves in alkalis with an extremely deep reddish-violet colour.

1 : 5-*Dibenzylaminoanthraquinone*, m. p. 225°, and 1 : 5-*di*-p-*chlorobenzylaminoanthraquinone*, m. p. 271—272°, are remarkable in that they are not converted into the corresponding dihydroanthraquinones by alkaline reducing agents. *Dibenzoyl*-1 : 5-*dibenzylaminoanthraquinone*, $C_{42}H_{30}O_4N_2$, m. p. 293°, prepared from 1 : 5-dibenzylaminoanthraquinone and benzoyl chloride at 90—100°, crystallises in red leaflets. C. S.

Relation between Molecular Constitution and Odour. Géza Austerweil and G. Cochin (*Compt. rend.*, 1910, 150, 1693—1695).—Citronellol, 1-methylcitronellol, and 1 : 1-*dimethylcitronellol* have distinct rose-like odours. The latter compound was obtained by oxidising 1-methylcitronellol and treating the resulting ketone by Grignard's method; it has b. p. 113—116°/24 mm., $[\alpha]_D$ −11°38′. 1-*Ethylcitronellol*, b. p. 125—130°/22 mm., $[\alpha]_D$ −11°26′, and 1 : 1-*diethylcitronellol*, b. p. 119—123°/20 mm., $[\alpha]_D$ −13°25′, have well-marked, rose-like odours. The odour is less distinct in 1-*propylcitronellol*, b. p. 118—122°/22 mm., and 1-*butylcitronellol*, b. p. 105—108°/16 mm. Introduction of a phenyl group intensifies the odour; 1-*phenylcitronellol* has b. p. 102—104°/12 mm.

An odour of roses appears to be associated with the presence of the group $-CH_2\cdot CRR'\cdot OH$; the presence of an ethylenic linking also appears to be essential. W. O. W.

A New Tertiary Menthol; Conversion of Pinene into Menthene. Auguste Béhal (*Compt. rend.*, 1910, 150, 1762—1765).—Haller and Martine (Abstr., 1905, i, 533) obtained hexahydrocymene by the reduction of terpineol; employing the same method, but under different conditions, the present author has converted terpineol into a tertiary *menthol*, $CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>CH\cdot CMe_2\cdot OH$. The product is optically inactive, and does not appear to be a mixture of *cis*- and *trans*-isomerides; it has b. p. 99—100°/17 mm., 206—208° under atmospheric pressure; D^{20} 0·912; n_D 1·46874. The *phenylurethane* has m. p. 94—95°; the *acetate* has b. p. 104°/16 mm. Acetic acid in presence of sulphuric acid transforms the menthol into $\Delta^{4(8)}$-menthene (Wallach, Abstr., 1905, i, 407; Auwers, this vol., i, 122). Oxidation with mercuric oxide and iodine, followed by treatment with silver nitrate, converts this hydrocarbon into menthone. W. O. W.

Constitution of Fenchone. Louis Bouveault and F. Levallois (*Bull. Soc. chim.*, 1910, [iv], 7, 542—548).—A résumé of work already published (Abstr., 1908, i, 193). The fenchone used was isolated by fractional distillation from the crude fenchone obtained from fennel oil. On treatment with sodamide until no further action took place, a residue containing camphor was obtained. T. A. H.

Constitution of Fenchone. II. Louis Bouveault and F. Levallois (*Bull. Soc. chim.*, 1910, [iv], 7, 683—687).—A résumé of

work already published in part (Abstr., 1908, i, 193; 1909, i, 497, 595). The following new data are given. Dihydrofencholenic acid, b. p. 162—165°/22 mm., obtained by hydrolysis of the amide with 30% potassium hydroxide in alcohol, does not solidify when pure (compare Semmler, Abstr., 1906, i, 681). The *chloride* has b. p. 105°/20 mm. The *anhydride*, b. p. 205—210°/20 mm., D^4 0·9841, obtained by warming the acid with acetic anhydride, is a colourless, thick liquid.

Dihydrofencholenamide, $C_9H_{17}\cdot CO\cdot NH_2$, on treatment with bromine and potassium hydroxide, gives di*apo*fenchylcarbamide,

$$CO(NH\cdot C_9H_{17})_2$$

(Abstr., 1908, i, 193), but if the alkali is replaced by sodium methoxide, the corresponding *methylurethane*, $C_{11}H_{21}O_2N$, b. p. 142°/23 mm., a colourless liquid of pleasant odour, is obtained. This is very stable to alkalis, but on prolonged heating with 30% potassium hydroxide in alcohol at 150° it furnishes apo*fenchylamine*,

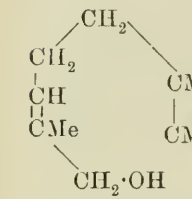
$$\begin{matrix} NH_2\cdot CMe{-}CO \\ | \qquad\quad > CHPr^{\beta}, \\ CH_2\cdot CH_2 \end{matrix}$$

b. p. 68°/18 mm. or 173°/760 mm., which has a strong odour and rapidly absorbs carbon dioxide, forming a snow-white mass. The corresponding *carbamide*, $C_9H_{17}\cdot NH\cdot CO\cdot NH_2$, m. p. 129—130°, crystallises in slender needles from acetic acid. T. A. H.

Constituents of Ethereal Oils. Further Degradation of Noreksantalic Acid. Friedrich W. Semmler and B. Zaar (*Ber.*, 1910, **43**, 1890—1892. Compare this vol., i, 495, and following abstract).—Methyl noreksantalate is converted by sodium and alcohol into *noreksantalol*, $C_{11}H_{18}O$, b. p. 114—117°/10 mm., D^{20} 0·9958, n_D 1·49049, α_D −0·7° (100 mm. tube), a benzene solution of which is oxidised by potassium dichromate and dilute sulphuric acid to *noreksantalal*, $C_{11}H_{16}O$, b. p. 92—94°/11 mm., D^{20} 0·9964, n_D 1·48301, α_D −30·8° (100 mm. tube), the *semicarbazone* of which has m. p. 224°. The CHO group of the aldehyde must be attached to a methylene group, because enol-*noreksantalal acetate*, $C_{11}H_{15}\cdot OAc$, b. p. 110—113°/10 mm., D^{20} 1·0270, n_D 1·48374, α_D −25·6° (100 mm. tube), obtained from the aldehyde, acetic anhydride, and sodium acetate, is oxidised in acetone solution by potassium permanganate to teresantalic acid, $C_{10}H_{14}O_2$. The formation of this acid, which contains 10 atoms of carbon, is another proof that the compounds of the noreksantalic acid series contain 11 atoms of carbon; numbers of the eksantalic acid series contain 12 atoms of carbon. In all three series occurs the same tricyclic system as is present in α-santalol. C. S.

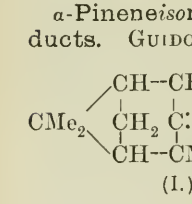
Constituents of Ethereal Oils. Constitutions of the α-Santalol and of the α-Santalene Series, and of Sesquiterpene Alcohols and of Sesquiterpenes. Friedrich W. Semmler (*Ber.*, 1910, **43**, 1893—1898).—"Santalol," obtained by distilling oil of sandel-wood with steam, converting the oil in the distillate into the hydrogen phthalate, and hydrolysing the ester, is a mixture of two

primary alcohols: $C_{15}H_{24}O$, which can be tolerably satisfactorily separated by repeated fractionation into α-santalol, b. p. 159—160°/10 mm., D^{20} 0·978, n_D 1·498, α_D 1° (100 mm. tube), and β-santalol, b. p. 167—168°/10 mm., D^{20} 0·9715, n_D 1·509, α_D −42° (100 mm. tube). The molecular refraction of the "santalol," regenerated from the hydrogen phthalates, indicates the presence therein of a singly unsaturated tricyclic alcohol and a doubly unsaturated dicyclic alcohol. The assumption that the former is α-santalol and the latter β-santalol is justified by the results of oxidising "santalol." Oxidation by potassium permanganate gives tricyclic eksantalic acid, $C_{12}H_{18}O_2$, and oxidation by ozone gives tricyclic eksantalal, $C_{12}H_{18}O$; the yields of the acid and of the aldehyde are best in the lower-boiling fractions, that is, those rich in α-santalol. Eksantalal has been converted into teresantalic acid (preceding abstract), the constitution of which is known. The author gives reasons for assigning to teresantalic acid a constitution based on the camphor type, not on the camphene type. Consequently, eksantalal, eksantalic acid, and therefore the sesquiterpene alcohol, α-santalol, have constitutions based on the camphor type. The last-mentioned alcohol has the annexed constitution.

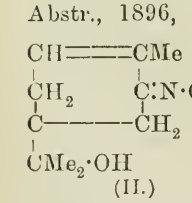


C. S.

α-Pinene*iso*nitroamineoxime and Its Decomposition Products. Guido Cusmano (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 747—753. Compare this vol., i, 182).—Nitrous acid reacts with the hydroxylamino-group of α-pinenehydroxylamineoxime, forming the *iso*nitroamineoxime, I, which is fairly stable when dry. When suspended in water and heated on the water-bath, however, it is converted into hydroxydihydrocarvoxime, II (compare Wallach, Abstr., 1896, i, 571), and nitrous oxide. A similar decomposition is effected by dilute acetic acid. Alkalis act differently, however, for they yield nitrous acid, nitrosopinene, and hydroxypinocamphoneoxime, III (the oxime of pinene hydrate). A substance, m. p. 70—80°, is also formed, but it is not crystalline. Since pinene*iso*nitroamineoxime yields hyponitrous acid (or nitrous oxide and water), however, it may be decomposed; it appears that the substance reacts as though it had the formula IV (compare this vol., i, 182).

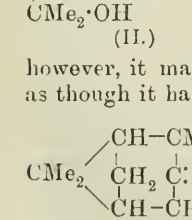


(I.)



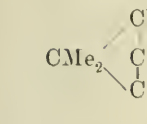
(II.)

α-Pinene*iso*nitroamineoxime is obtained by the action of an aqueous solution of sodium nitrite on an aqueous solution of the hydrochloride or sulphate of pinene-*o*-hydroxylamineoxime; it forms large, colourless prisms, m. p. 127° (decomp.), dissolves in alkali carbonates, gives Liebermann's reaction, and a wine-red coloration



(III.)

with ferric chloride. The *sodium* salt, prepared with the aid of sodium ethoxide, decomposes at 92—95°. The *hydroxylamine* salt,



(IV.)

$C_{10}H_{17}O_2N_2 \cdot NH_2 \cdot OH$,

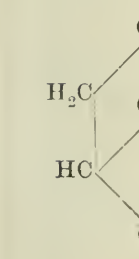
crystallises in lustrous prisms, m. p. 110° (decomp.); it reduces Fehling's solution in the cold, and barely shows Liebermann's reaction. o-*Hydroxypinocamphoneoxime*, which is best obtained (yield 20%) by the slow decomposition of the sodium salt of the *iso*nitroamine at the ordinary temperature, crystallises in lustrous, rhombic prisms, m. p. 128° (softening a few degrees previously). The substance resists prolonged boiling with aqueous or alcoholic solutions of alkaline hydroxides, but it is at once attacked by acids. When treated with hydrochloric acid, even in the cold, it loses its oximic group. Dilute acetic acid does not affect the oximic group, but converts the compound completely into hydroxydihydrocarvoxime.

R. V. S.

Sesquiterpenes. IV. Ernst Deussen [with Hans Philipp] (*Annalen*, 1910, 374, 105—120. Compare Abstr., 1909, i, 813).—A. *Gurjun balsam oil.*—This oil varies considerably in composition, and contains at least two distinct sesquiterpenes, named provisionally, α- and β-gurjunene. *α-Gurjunene* is a strongly lævorotatory oil, b. p. about 119°/12 mm., and is probably a dicyclic sesquiterpene. *β-Gurjunene* is a slightly dextrorotatory oil, b. p. about 122·5—123·5°/12 mm., and is probably a tricyclic compound. Both sesquiterpenes, when oxidised by potassium permanganate, yield a *ketone*, $C_{15}H_{24}O$, a colourless oil, b. p. 175—178°/12 mm., α_D +120—130°, D 1·0160, n_D 1·5303; the *oxime* of the ketone is pale yellow, and has b. p. 204°/12 mm. Gurjun balsam oil, when treated with hydrogen chloride and subsequently with anhydrous sodium acetate and glacial acetic acid, yields iso*gurjunene*, a dicyclic sesquiterpene, b. p. 129·5—132°/12 mm., which when oxidised does not yield a ketone forming a crystalline semicarbazone.

B. "*Caryophyllene.*"—The substance m. p. 125—125·5°, which was isolated from the mother liquor obtained in the preparation of α-caryophyllene nitrosochloride (*loc. cit.*), is shown to be a *nitrosoethoxycaryophyllene*, $OEt \cdot C_{15}H_{24} \cdot NO$.

Monoterpenes.—I. The substance obtained by the action of sodium methoxide on pinene nitrosochloride (*loc. cit.*) is *oximinomethoxyhydropinene* (annexed formula). It is converted (1) by phenyl carbimide into the corresponding *urethane*,



$OMe \cdot C_{10}H_{15} \cdot NO \cdot CO \cdot NHPh$,

which crystallises in rosettes of needles, m. p. 102°, and (2) by an alcoholic solution of hydrogen chloride into *i*-chlorohydrocarvoxime.

Nitrosopinene, when treated with phenylcarbimide, yields the corresponding *urethane*, $C_{17}H_{20}O_2N_2$, m. p. 101—102°.

II. Pinene nitrosochloride as usually prepared, when washed with ethyl alcohol, yields a dextrorotatory solution in chloroform, and when treated with benzylamine yields a nitrolbenzylamine, together with a *substance* (pinenenitrolbenzylamine?) which crystallises in needles, m. p. 148—149°, $[\alpha]_D$ +96·7° (1·191% solution in ethyl acetate). The presence of an oximino-group in pinenenitrolbenzylamine is demonstrated by the formation of a *urethane*,

$$CH_2Ph\cdot NH\cdot C_{10}H_{15}{:}NO\cdot CO\cdot NHPh,$$

m. p. 189·5—190° (decomp.), when it is treated with phenylcarbimide.

W. H. G.

Scutellarin. Guido Goldschmiedt and Ernst Zerner (*Monatsh.*, 1910, 31, 439—491. Compare Goldschmiedt and Molisch, Abstr., 1902, i, 48).—An amplification of work already recorded. The formula $C_{21}H_{20}O_{12}$, previously attributed to scutellarin, is altered to $C_{21}H_{18}O_{12}$, as a consequence of further analysis and of its hydrolysis to scutellarein and glycuronic acid. Scutellarin is shown to be homogeneous by extraction with methyl alcohol, whereby only a slight black powder, chiefly inorganic, remains; the substance in the alcoholic solution is fractionally crystallised, yielding fractions having practically the same properties. The colour reaction with α-naphthol and sulphuric acid is shown to be characteristic of glycuronic acid. By titration with *N*/10-potassium hydroxide and phenolphthalein, by estimating the carbon dioxide liberated from barium carbonate by scutellarin, and by the analysis of the barium salt, scutellarin is proved to contain one carboxyl and one phenolic hydroxyl group. The acetate, m. p. 263—265° (decomp.), contains five acetyl groups, and regenerates scutellarin by hydrolysis. When oxygen is passed for four days into a solution of scutellarin in 25% potassium hydroxide, the ethereal extract of the resulting solution contains *p*-hydroxyacetophenone.

The hydrolysis of scutellarin is best effected by adding concentrated sulphuric acid to a rapidly stirred suspension of finely powdered scutellarin in water until solution is complete, and then pouring the mixture into cold water. The operation requires only thirty to forty seconds, a quantitative precipitate of scutellarein is obtained, and the filtrate contains glycuronic acid.

Scutellarein, $C_{15}H_{10}O_6$, is undoubtedly a flavone derivative by reason of its behaviour as a mordant dye, its property of forming salts with metals or acids, and the nature of its products of decomposition by alkalis. It is oxidised by boiling 14—15% nitric acid to picric, oxalic, and 3 : 5-dinitro-4-hydroxybenzoic acids. By acetylation it yields a *tetra-acetate*, $C_{15}H_6O_6(OAc)_4$, m. p. 235—237°.

Methylation by ethereal diazomethane yields *scutellarein trimethyl ether*, $C_{15}H_7O_3(OMe)_3$, m. p. 189—190°, whilst the action of methyl iodide and methyl-alcoholic potassium hydroxide results in the formation of the trimethyl ether, together with a small amount of a *tetramethyl ether*, m. p. 158—160°.

The hydrolysis of scutellarein by boiling 12% potassium hydroxide or by fusion with potassium hydroxide yields *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid, and a substance which gives the pine-shaving reaction of phloroglucinol.

The preceding results are explained by regarding scutellarein as 1 : 3 : 4 : 4′-(or 1 : 2 : 3 : 4′-)tetrahydroxyflavone, and scutellarin provisionally as $R{\cdot}O{\cdot}CH{\cdot}[CH{\cdot}OH]_2{\cdot}CH{\cdot}CH(OH){\cdot}CO_2H$, where R represents the scutellarein residue. C. S.

Cornin, the Bitter Principle of Cornus Florida. Emerson R. Miller (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, 7, xlii—xliii).—The best yields are obtained from the root-bark. It crystallises in colourless, silky needles or rectangular plates, m. p. 181°, and has neither basic nor acidic properties. Its aqueous solutions do not yield precipitates with silver nitrate or lead subacetate, but when kept for some time they reduce Fehling's solution, and when heated with a little alkali reduce Fehling's solution immediately. The aqueous solution also gives Pettenkofer's test for dextrose. It appears to be a glucoside with the composition represented by the formula $C_{17}H_{24}O_{10}$ or $C_{16}H_{21}O_9{\cdot}OMe$. J. J. S.

Action of Phosphorus Pentachloride on Picrotin. Paul Horrmann (*Ber.*, 1910, 43, 1903—1907).—Phosphorus pentachloride acts as a dehydrating agent on picrotin in boiling chloroform, converting it into *anhydropicrotin*, $C_{15}H_{16}O_6$, m. p. 317° (decomp.), which does not reduce Fehling's solution or ammoniacal silver oxide solution, forms a *benzoate*, $C_{22}H_{20}O_7$, m. p. 250°, an *acetate*, $C_{17}H_{18}O_7$, m. p. 237°, and a *diacetate*, $C_{19}H_{20}O_8$, m. p. 192·5°, and dissolves in hot *N*/10-sodium hydroxide, the solution after acidification yielding *anhydropicrotinic acid*, $C_{15}H_{18}O_7{,}H_2O$, which decomposes at 221°, or in the anhydrous state at 233°.

The chloroform mother liquor contains a halogenated substance, which by prolonged boiling with methyl alcohol is converted into a *substance*, $C_{16}H_{21}O_8P$, m. p. 211°, which has not been further examined. C. S.

Picrotoxin. Francesco Angelico (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 473—480. Compare this vol., i, 404). The reduction of α-picrotinic acid with hydriodic acid and red phosphorus yields, not only the acid, $C_{15}H_{18}O_4$, previously described (*loc. cit.*), but also a *ketone*, which from the composition of its *oxime* should have the formula $C_{14}H_{16}O_3$. When picrotoxin is heated with hydrochloric acid (of D 1·19, diluted with an equal volume of water) in a sealed tube for five hours at 170—180°, it also gives a *ketone*, $C_{14}H_{15}ClO_3$, which results from the substitution of an hydroxyl group by chlorine and loss of carbon dioxide. Picrotin yields the same substance, losing at the same time the molecule of water by which its formula differs from that of picrotoxin, so that both substances must contain the same nucleus. The ketone crystallises in small needles, m. p. 114—115°; it is insoluble in alkalis, and it forms an osazone, m. p. 196°, which does not contain halogen.

In order to obtain an indication of the presence of an aromatic nucleus, which from other reasons is probable, picrotinic acid, $C_{15}H_{18}O_4$, was nitrated with a mixture of equal volumes of concentrated

sulphuric acid and nitric acid (D 1·48) A *nitro*-derivative, $C_{13}H_{15}O_5N$, was obtained; it crystallises in pale yellow needles, m. p. 166°, and is very stable towards oxidising agents. A small quantity of a *substance* insoluble in alkali was also formed; it had m. p. about 110°. When the above nitro-derivative was reduced with ammonium sulphide, another *nitro*-compound was formed, m. p. 173° (previously softening).

R. V. S.

Method of Preparing Dimethylpyrone. Zdenko H. Skraup and J. Priglinger (*Monatsh.*, 1910, 31, 363—369).—A mixture of 95 grams of acetic anhydride and 20 c.c. of sulphuric acid is boiled for four hours, and distilled as completely as possible in a vacuum. The solution of the residue in saturated ammonium sulphate is faintly basified by ammonium hydroxide, filtered, and repeatedly extracted with benzene. The extracts contain about 4 grams of 2 : 6-dimethylpyrone, m. p. 132—133°. It is shown that the pyrone does not exist as such in the acetic anhydride.

In still poorer yield dimethylpyrone is obtained by heating acetic anhydride with phosphoric oxide, or by heating a mixture of acetyl chloride, glacial acetic acid, and sulphuric acid.

Dimethylpyrone is easily converted into lutidone by dissolving it in a little water, saturating the solution with ammonia, and heating the mixture in a sealed tube for eight hours in a water-bath. C. S.

Synthesis of 2:3-Dihydroxyflavone. J. Reigrodski and Josef Tambor (*Ber.*, 1910, 43, 1964—1968).—Hydroxyquinol trimethyl ether reacts with acetyl chloride in the presence of aluminium chloride and carbon disulphide, yielding 2 : 4 : 5-*trimethoxyacetophenone*, $C_6H_2(OMe_3)\cdot COMe$, which crystallises from alcohol in small, colourless needles, m. p. 102—103°. The ketone reacts with methyl benzoate and sodium (granulated) at 115—120°, yielding 2 : 4 : 5-*trimethoxybenzoylacetophenone*, $COPh\cdot CH_2\cdot CO\cdot C_6H_2(OMe)_3$, which crystallises in small, ochre-yellow prisms, m. p. 105°. It gives a dark green coloration with ferric chloride, and when boiled for four hours with concentrated hydriodic acid yields 2 : 3-*dihydroxyflavone*, $C_6H_2(OH)_2<\begin{matrix}O—CPh\\ \|\\ CO\cdot CH\end{matrix}$, which crystallises from dilute alcohol in colourless, microscopic prisms containing $1H_2O$, and with m. p. 135° (decomp.). Its *diacetyl* derivative, $C_{19}H_{14}O_6$, crystallises in thin needles, m. p. 195°, and its *dimethyl ether*, $C_{17}H_{14}O_4$, in slender, colourless needles, m. p. 189°.

2 : 4 : 5-Trimethoxyacetophenone condenses with aldehydes, yielding chalkone derivatives (Abstr., 1904, i, 426). With benzaldehyde it yields 2 : 4 : 5-*trimethoxychalkone*, $C_6H_2(OMe)_3\cdot CO\cdot CH{:}CHPh$, which crystallises in canary-yellow needles, m. p. 113—114°. Its solution in concentrated sulphuric acid is orange-coloured, and its *dibromide*, $C_{18}H_{18}O_4Br_2$, crystallises in pale yellow, prismatic plates, m. p. 148° (decomp.).

2-*Hydroxy*-2′ : 4′ : 5′-*trimethoxybenzylideneacetophenone* (2-*hydroxy*-2′ : 4′ : 5′-*trimethoxychalkone*), $OH\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot C_6H_2(OMe)_3$, obtained by condensing salicylaldehyde with trimethoxyacetophenone

and alkali, crystallises in green needles, m. p. 159—160° (decomp.). The *acetyl* derivative, $C_{20}H_{20}O_6$, crystallises in glistening, golden needles, and the *acetyl-dibromide*, $C_{20}H_{20}O_6Br_2$, forms colourless needles, m. p. 132° (decomp.). The latter compound reacts with alcohol and concentrated potassium hydroxide solution, yielding 2′ : 4′ : 5′-*trimethoxy*-1-*benzoylcoumarone*, $C_6H_4<\overset{O}{\underset{CH}{>}}C\cdot CO\cdot C_6H_2(OMe)_3$, which crystallises from dilute alcohol in prismatic, yellow needles, m. p. 125°. Its solution in concentrated sulphuric acid is orange-coloured.

J. J. S.

1 : 3-Dimethoxycoumaranone. H. Dumont and Josef Tambor (*Ber.*, 1910, 43, 1969—1971).—*α-Bromophloroacetophenone trimethyl ether* (1 : 3 : 5-*trimethoxy*-1-*bromoacetylbenzene*), $C_6H_2(OMe)_3\cdot CO\cdot CH_2Br$, obtained by the Friedel-Crafts synthesis from bromoacetyl bromide and phloroglucinol trimethyl ether, crystallises in colourless needles, m. p. 126°, and when boiled with alcoholic potassium acetate (compare Blom and Tambor, Abstr., 1905, i, 916) yields 1 : 3-dimethoxycoumaranone, $C_6H_2(OMe)_2<\overset{O}{\underset{CO}{>}}CH_2$, which is identical with Friedländer and Schnell's dimethoxyketocoumaran (Abstr., 1898, i, 24).

1 : 3 : 2′ : 3′-*Tetramethoxybenzylidenecoumaranone*,

$$C_6H_2(OMe)_2<\overset{O}{\underset{CO}{>}}C:CH\cdot C_6H_3(OMe)_2,$$

obtained by condensing 1 : 3-dimethoxycoumaranone with *o*-veratraldehyde and alkali, crystallises in yellow needles, m. p. 166°. Its solution in concentrated sulphuric acid is dark orange-coloured.

The isomeric 1 : 3 : 2′ : 4′-*tetramethoxy*-compound, obtained from 1 : 3-dimethoxycoumaranone and 2 : 4-dimethoxybenzaldehyde, forms yellow needles, m. p. 209° ; its solution in concentrated sulphuric acid is blood-red. The 1 : 3 : 3′ : 4′-*tetramethoxy*-derivative has m. p. 175°, and also yields a blood-red solution in sulphuric acid. J. J. S.

Sulphur Derivatives of Ethyl Chlorocyanoacetoacetate. Erich Benary (*Ber.*, 1910, 43, 1943—1956. Compare Abstr., 1908, i, 600).—Ethyl γ-chloro-α-cyanoacetoacetate reacts with an aqueous 15% solution of potassium hydrogen sulphide, yielding crystals of ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate,

$$S<\overset{CH_2}{\underset{C(:NH)\cdot CH\cdot CO_2Et}{}}\!\!>CO$$

and ethyl thiobiscyanoacetoacetate, $S[CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et]_2$, which remains dissolved in the alkaline solution, and is precipitated on the addition of dilute sulphuric acid.

Ethyl 2-*imino*-4-*ketotetrahydrothiophen*-3-*carboxylate* crystallises in flat, silvery needles, m. p. 219—220° (decomp.), after turning brown at 200°. It dissolves in dilute sodium hydroxide solution, but is rapidly decomposed. The *diacetyl* derivative, $C_{11}H_{13}O_5NS$, crystallises in hard lamellæ, m. p. 108—109°. When the ester is dissolved in 10% sodium hydroxide solution, and kept for twenty-four hours, it

yields *3-cyano-2 : 4-diketotetrahydrothiophen*, $S<\begin{matrix}CH_2\cdot C\cdot OH\\ \|\\ CO-C\cdot CN\end{matrix}$, which is probably formed by the rupture of the sulphur ring and its subsequent closing by the elimination of ethyl alcohol. The product crystallises with $1H_2O$, has m. p. 181—182° (decomp.), is a monobasic acid, and hence has the keto-enolic constitution. The *silver* salt, $C_5H_2O_2NSAg$, is sparingly soluble, and the acid, which dissolves readily in most solvents, is best purified by conversion into its *diacetyl* derivative, $C_9H_7O_4NS$, which forms colourless needles, m. p. 63—64°. *3-Cyano-2 : 4-diketo-5-benzylidenetetrahydrothiophen*,

$$CHPh:C<\begin{matrix}C(OH):C\cdot CN\\ |\\ S---CO\end{matrix},$$

obtained by condensing the ketone with benzaldehyde in the presence of sodium ethoxide, crystallises in pale yellow needles, m. p. 220° (decomp.), and forms a *sodium* salt, $C_{12}H_6O_2NSNa$, which separates as colourless crystals from alcohol. When boiled with excess of barium hydroxide solution for half an hour, the nitrile yields the bimolecular *compound*, $C_{20}H_{12}O_8N_4S_4$, as colourless needles, m. p. 198° (decomp.), after turning brown at 180°. It is sparingly soluble in water, and yields a *barium* salt, $(C_{20}H_5O_4N_2S_2)_2Ba$, as a colourless syrup which sets to a vitreous mass. When heated on the water-bath for a quarter of an hour with five times its weight of concentrated sulphuric acid, the nitrile takes up water and yields *2 : 4-diketotetrahydrothiophen-3-carboxylamide*, $S<\begin{matrix}CH_2\cdot C\cdot OH\\ \|\\ CO-C\cdot CO\cdot NH_2\end{matrix}$, which is deposited when the mixture is poured onto ice as a sparingly soluble, crystalline powder, m. p. 177—178° (decomp.). It yields a *potassium* salt, $C_5H_4O_3NSK$, which is sparingly soluble in alcohol. It has not been found possible to transform the nitrile or amide into the corresponding acid.

2-Imino-4-ketotetrahydrothiophen, $S<\begin{matrix}CH_2---C\cdot OH\\ \|\\ C(:NH)\cdot CH\end{matrix}$, obtained by heating the ketonic ester with twenty times its weight of fuming hydrochloric acid, crystallises from water in colourless needles, which turn brown at 190°, and decompose at 215°. Its aqueous solution is neutral, but it dissolves in both alkalis and dilute acids. With a chloroform solution of bromine, it yields the *3-bromo*-derivative, $S<\begin{matrix}CH_2---C\cdot OH\\ \|\\ C(:NH)\cdot CBr\end{matrix}$, which crystallises in brownish-coloured needles, m. p. 157°, and yields a *hydrobromide*. With nitrous acid it yields the *3-oximino*-derivative, $S<\begin{matrix}CH_2---CO\\ |\\ C(:NH)\cdot C:N\cdot OH\end{matrix}$, as violet needles, decomposing at 175°, and when this is reduced with zinc dust and acetic acid, *3-amino-2-imino-4-ketotetrahydrothiophen*, $S<\begin{matrix}CH_2---C\cdot OH\\ \|\\ C(:NH)\cdot C\cdot NH_2\end{matrix}$, is obtained as plates, which turn brown at 140°, and are completely decomposed at 174—175°. The *benzylidene* derivative of the amine, $C_{11}H_{10}ON_2S$, decomposes at 181°. The amine reacts with nitrous acid, yielding an *acid*, $C_4H_5O_2N_3S$, which decomposes at 200°, and forms a *lead* salt as a brown precipitate.

The imino-ketone reacts with warm formaldehyde solution, yielding *methylenebis-4-keto-2-iminotetrahydrothiophen*,

$$CH_2\left[C\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}C(OH)\text{—}CH_2\\ C(:NH)\cdot S\end{matrix}\right],$$

as colourless, soft, felted needles, which darken at 260°.

Ethyl thiobiscyanoacetoacetate crystallises from alcohol in glistening plates, m. p. 98—99°, and is the only product formed when hydrogen sulphide is passed into an alkaline solution of ethyl chlorocyanoacetoacetate. It yields a green precipitate with cupric acetate, is not hydrolysed by cold alkalis, but with concentrated sulphuric acid yields ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate and *α-carboxylamidotetronic acid*, $O<\begin{matrix}CH_2\cdot C\cdot OH\\ \|\\ CO\text{—}C\cdot CO\cdot NH_2\end{matrix}$, as colourless needles, m. p. 182—183° (decomp.).

Ethyl α-cyano-γ-thiocyanoacetoacetate,

$$NCS\cdot CH_2\cdot C(OH):C(CN)\cdot CO_2Et,$$

obtained by the action of potassium thiocyanate on an alkaline solution of ethyl chlorocyanoacetoacetate, crystallises in slender needles, m. p. 82—84°. It decomposes when left exposed to the air, and when left in contact with fuming hydrochloric acid for twenty-four hours yields ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate, but with cold concentrated sulphuric acid, it yields *ethyl α-cyano-γ-thiocarbamatoacetoacetate*, $NH_2\cdot CO\cdot S\cdot CH_2\cdot C(OH):C(CN)\cdot CO_2Et$, as soft needles, m. p. 155—156°.

Practically all the compounds with the exception of the original 2-imino-4-ketotetrahydrothiophencarboxylate give deep red colorations with ferric chloride, and exist in the enolic forms given above.

J. J. S.

Rotatory Power of Normal Quinine Hydrochloride. André and Leulier (*J. Pharm. Chim.*, 1910, [vii], **2**, 22).—Experiments show that the specific rotatory power of normal quinine hydrochloride increases with the dilution, whereas the French Codex states diametrically the opposite, namely, that it increases with the concentration of the solution. L. de K.

Action of Chlorine and Ammonia on Quinine. Ezio Comanducci (Pamphlet 12 pp.).—By the action of chlorine or other oxidising agents followed by ammonia on salts of quinine, a number of coloured compounds are produced. In addition to the thalleioquinine ($C_{15}H_{20}O_5N_2$), erythroquinine, rusioquinine ($C_{24}H_{60}O_{16}N_3$), melanoquinine ($C_{26}H_{36}O_{12}N_3$), and a colourless derivative previously known, the author has obtained a reddish-violet compound, rubroquinine, and a colourless substance, leucoquinine. From an examination of numerous quinine derivatives containing a phenolic hydroxyl group, the author comes to the conclusion that the production of these coloured substances depends on the presence of a phenolic group attached to a naphthalene or quinoline nucleus. Thalleioquinine is obtained as a green precipitate, m. p. 130°, by treating a quinine solution with chlorine water, and adding ammonia a few seconds

afterwards. On further treatment with chlorine water and ammonia, it yields a red *substance*, which contains chlorine. When the addition of ammonia is delayed about three times as long as in the case of thalleioquinine, and the ammonia added in two portions, *rubroquinine* is precipitated; it has m. p. 118—120°, is soluble in chlorine water, and is reprecipitated on adding ammonia. When a solution of quinine sulphate is treated with chlorine water for five minutes and then quickly with ammonia, a white precipitate, *leucoquinine*, is obtained. It has m. p. 138°, and is slightly soluble in chlorine water; on adding ammonia to the solution, a red precipitate is obtained. Rubroquinine and leucoquinine are soluble in acids.

R. V. S.

Constitution of Cinchonicine (Cinchotoxine). II. Derivatives and Salts of Ethyl-, Phenyl-, and α-Naphthyl-cincotoxol. Ezio Comanducci (*Rend. R. Accad. Sci. Fis. Mat. Napoli*, 1910, Reprint 11 pp. Compare Abstr., 1909, i, 409).—By the preparation of the derivatives described in this paper, it is established that the vinyl group, and secondary and tertiary nitrogen atoms of cinchonicine are present also in the cinchotoxoles, whilst the ketonic group has been converted into a tertiary alcoholic grouping.

Ethyl cinchotoxol hydrochloride, $C_{21}H_{28}ON_2,2HCl$, has m. p. 108—109° (sintering at 100°), and $[\alpha]_D^{15}$ +51·75°. The *platinichloride*, $C_{21}H_{28}ON_2,H_2PtCl_6,H_2O$, is a red, crystalline powder, m. p. 210°. The *aurichloride*, $C_{21}H_{28}ON_2,2HAuCl_4,3H_2O$, a yellow, crystalline powder, has m. p. 120—121°. The *picrate*,

$$C_{21}H_{28}ON_2,2C_6H_3O_7N_3$$

is prepared from the hydrochloride; it is a yellow powder, which sinters at 80°, and has m. p. 102°. When an insufficient quantity of picric acid is taken, a *picrate hydrochloride*, $C_{21}H_{28}ON_2,HCl,C_6H_3O_7N_3$, m. p. 98°, is obtained. The *tartrate*, $C_{21}H_{28}ON_2,C_4H_6O_6,H_2O$, sinters at 95°, and melts at 107° (decomp.). The *methiodide*, $C_{21}H_{28}ON_2,MeI$, forms small, reddish-brown crystals, m. p. 138—140°. The *nitroso*-derivative, $C_{21}H_{27}ON_2{\cdot}NO$, has m. p. 147—150° (decomp.); it gives Liebermann's reaction. The *benzoyl* derivative, $C_{21}H_{27}ON_2{\cdot}COPh$, forms white, crystalline scales, m. p. 114°. The *bromine* derivative, $C_{21}H_{28}ON_2Br_2$, is obtained by mixing chloroform solutions of bromine and the base; it is a reddish-white powder, m. p. 190° (sintering at 150°).

Phenylcinchotoxol hydrochloride, $C_{18}H_{22}N_2{\cdot}CPh{\cdot}OH,2HCl$, sinters at 75°, and melts at 86—100°; it has $[\alpha]_D^{15}$ +21·09°. The *platinichloride*, $C_{25}H_{28}ON_2,H_2PtCl_6,H_2O$, is a yellow powder, which decomposes above 200°. The *aurichloride*, $C_{25}H_{28}ON_2,2HAuCl_4$, forms yellow tablets, which sinter at 70°, and melt at 113—115°. The *picrate*,

$$C_{25}H_{28}ON_2,C_6H_3O_7N_3,$$

is a yellow powder, m. p. 105°. The *tartrate*,

$$C_{25}H_{28}ON_2,C_4H_6O_6,3\tfrac{1}{2}H_2O,$$

forms tablets or prisms, m. p. 225° (becoming brown at 180°); the anhydrous substance has m. p. 240°. The *methiodide*, $C_{25}H_{28}ON_2,MeI$, has m. p. 127—129° (sintering at 120°). The *nitroso*-derivative, $C_{25}H_{27}ON_2{\cdot}NO,HCl$, has m. p. 147—149°, and decomposes at 150°; it

gives Liebermann's reaction. The *bromo*-derivative, $C_{25}H_{28}ON_2Br_2$, sinters at 150° and melts at 195°. The *benzoyl* derivative,

$$C_{25}H_{27}ON_2\cdot COPh,$$

forms red scales, which sinter at 165°, and melt at 178° (decomp.). When phenylcinchotoxole is treated with a 2% solution of potassium permanganate at 2°, formic acid is produced, in addition to a yellow, crystalline *substance* of slightly acid reaction, which has m. p. 188° (becoming brown at 167°).

α-Naphthylcinchotoxol hydrochloride, $C_{18}H_{22}N_2{:}C(C_{10}H_7)\cdot OH,2HCl$, is a deliquescent, reddish-brown mass, m. p. 71—85° (sintering at 60°); it has $[\alpha]_D^{15}$ +49·6°. The *platinichloride*, $C_{29}H_{30}ON_2,H_2PtCl_6,H_2O$, forms a yellow, amorphous powder, which becomes brown, and decomposes at 330°. The *aurichloride*, $C_{29}H_{30}ON_2,2HAuCl_4,H_2O$, is a yellow powder, m. p. 144—145° (decomp.). The *picrate hydrochloride*,

$$C_{29}H_{30}ON_2,C_6H_3O_7N_3,HCl,$$

sinters at 97°, and has m. p. 101° (decomp.). The *methiodide*,

$$C_{29}H_{30}ON_2,MeI,$$

is a reddish-brown substance, m. p. 140°. R. V. S.

Constitution of Cinchonicine (Cinchotoxine). III. Chloroethyl- and Chlorophenyl-cinchotoxile. Ezio Comanducci (*Rend. R. Accad. Sci. Fis. Mat. Napoli*, 1910, Reprint 5 pp. Compare preceding abstract).—By the action of phosphoryl chloride and phosphorus pentachloride in chloroform solution, the alcoholic hydroxyl group of the *R*-cinchotoxols (compare Abstr., 1909, i, 409) may be replaced by chlorine; the substances so obtained are termed by the author chloro-*R*-cinchotoxiles.

Chloroethylcinchotoxile, $C_{18}H_{21}N_2{:}CEtCl$, is a reddish-brown powder, which sinters at 85°, and melts at 115—117°. The *platinichloride*, $C_{21}H_{26}N_2Cl,H_2PtCl_6$, forms a reddish-yellow powder, which becomes brown at 210°. The *picrate*, $C_{21}H_{26}N_2Cl,C_6H_3O_7N_3$, is a yellow powder, which becomes brown at 115°, and melts at 130°.

Chlorophenylcinchotoxile forms dark yellow scales, m. p. 148—155°. The *platinichloride*, $C_{25}H_{26}N_2Cl,H_2PtCl_6$, becomes brown, and decomposes at 220°. The *picrate*, $C_{25}H_{26}N_2Cl,C_6H_3O_7N_3$, has m. p. 121—122°. By the action of alcoholic potassium hydroxide on the chlorophenyl-derivative, a *compound* was obtained, which had m. p. 62—63°, and was free from chlorine. R. V. S.

Strychnine and Brucine. Roberto Ciusa and G. Scagliarini (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 555—561. Compare Beckurts, Abstr., 1905, i, 918, and Martin, Abstr., 1904, i, 446).—By the action of bromine on a solution of strychnine in glacial acetic acid, a *dibromide*, $C_{21}H_{22}O_2N_2Br_2$, is produced. The substance crystallises from alcohol in rosettes of colourless needles, m. p. 122°, but by repeated crystallisation from alcohol, or by heating above its m. p., it is converted into another, more stable form, which forms large, colourless, monoclinic crystals, m. p. 260°. In the preparation of the dibromide the formation of a *perbromide*, $C_{21}H_{22}O_2N_2Br_3$, may occur. When the dibromide is boiled with water, it dissolves, and the solution on cooling

deposits the *hydrobromide* of the monobromostrychnine, m. p. 222°, of Beckurts (*loc. cit.*) and Martin (*loc. cit.*). This monobromostrychnine does not lose bromine even when heated with alcoholic potassium hydroxide in a sealed tube. With chloroanil in ethereal-alcoholic solution it gives a violet coloration, and with concentrated sulphuric acid and potassium dichromate it yields a fugitive, reddish-violet coloration. When it is treated with bromine, a *perbromide*, $C_{21}H_{22}O_2N_2Br_6,H_2O$, is formed, which crystallises in golden-yellow needles, which on heating darken at 200° with loss of bromine. On heating this compound with water or with thiosulphate solution, a *substance* is obtained containing 28·35—28·49% bromine. From the methyl-alcoholic mother liquors of the perbromide, a crystalline *hydrobromide* of the composition $C_{21}H_{21}O_2N_2Br,Br_2,HBr,H_2O$ can be obtained. From the mother liquor of this substance the addition of potassium hydroxide precipitates the *dibromide* of monobromostrychnine; it could not be crystallised.

Whilst strychnine and monobromostrychnine reduce acid solutions of permanganate at once, the dibromides of these substances only do so after a time. Monobromostrychnine and the two dibromides do not react with hydroxylamine or with *p*-nitrophenylhydrazine. The authors consider that the above behaviour may be explained by the presence of the grouping $X\lessdot\begin{matrix}CH\\ \|\\ C\end{matrix}$ in strychnine, the constitutions of the above derivatives being represented by the following formulæ:

$$C_{19}H_{21}O_2N_2\lessdot\begin{matrix}CHBr\\ |\\ CBr\end{matrix}, \quad C_{19}H_{21}O_2N_2\lessdot\begin{matrix}CBr\\ \|\\ C\end{matrix},HBr,$$

$$C_{19}H_{21}O_2N_2\lessdot\begin{matrix}CBr\\ \|\\ C\end{matrix}, \quad C_{19}H_{21}O_2N_2\lessdot\begin{matrix}CBr_2\\ |\\ CBr\end{matrix}.$$

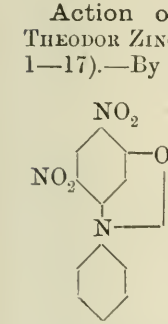
R. V. S.

Amine Peroxides of Brucine and Strychnine. Gustav Mossler (*Monatsh.*, 1910, 31, 329—345).—When brucine is heated with 3% hydrogen peroxide on the water-bath and the solution is concentrated in a vacuum, crystals of a *peroxide* containing two atoms of active oxygen are obtained, which contain $4H_2O$ when slowly crystallised, $3H_2O$ when rapidly crystallised, and $2H_2O$ when dried in a vacuum. Another mol. of H_2O can be expelled at 100° or by crystallisation from alcohol, but the elimination of the remaining H_2O is accompanied by the loss of the active oxygen. The peroxide has m. p. 202—203° (decomp.), the air-dried crystals softening at 115—125°, those dried in a vacuum at 135°. In aqueous solution the peroxide dissociates into brucine oxide and hydrogen peroxide, but it dissolves without decomposition in non-dissociating solvents, alcohol, or chloroform. An aqueous solution, warmed with platinum black, evolves oxygen and yields brucine oxide, which can be reconverted into the peroxide by hydrogen peroxide. In 3% hydrogen peroxide the substance has $[\alpha]_D$ −5·12°, and yields with dilute sulphuric acid mainly the sulphate of brucine oxide. Sulphurous acid eliminates the active oxygen from the peroxide, leaving a mixture of brucine and *allo*-brucine.

Strychnine peroxide is obtained with some difficulty from strychnine and 14% hydrogen peroxide. The air-dried crystals contain $4H_2O$, two

of which are lost in a vacuum, the substance then having m. p. 178° (decomp.), and containing two atoms of active oxygen. The peroxide is almost completely dissociated in aqueous solution. In 95% alcohol it has $[\alpha]_D$ 9·7°. C. S.

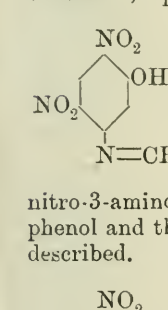
Action of Pyridine on 1 : 3-Dichloro-4 : 6-dinitrobenzene. Theodor Zincke and G. Weispfenning (*J. pr. Chem.*, 1910, [ii], 82, 1—17).—By the action of hot pyridine on 1 : 3-dichloro-4 : 6-dinitrobenzene, Reitzenstein and Rothschild (Abstr., 1906, i, 454) obtained, together with dinitrophenyldipyridinium dichloride, a yellow condensation product, to which they assigned the constitution



$$C_6H_2(NO_2)_2<\begin{matrix}C_5NH_5\cdot O\\ C_5NH_5\cdot O\end{matrix}>C_6H_2(NO_2)_2.$$

This substance is now shown to be a betaine anhydride (annexed constitution), produced from the dinitrophenyldipyridinium dichloride by the action of the water present. It can also be prepared by the action of sodium nitrite on an aqueous solution of the dichloride, and by heating pyridine and 3-chloro-4 : 6-dinitrophenol at 100°. The addition of alcohol to solutions of the substance in moderately concentrated acids precipitates well characterised salts, of which the *chloride*, *chromate*, *platinichloride*, *nitrate*, and *sulphate* are described. It is converted into pyridine and dinitroresorcinol by 20% hydrochloric acid at 170°, and into pyridine and chlorodinitrophenol by hydrogen chloride in glacial acetic acid at 150°.

The action of excess of 2*N*-sodium hydroxide on an aqueous solution of the chloride of the condensation product yields a red substance, $C_{11}H_9O_6N_3$, which has not the constitution given to it by Reitzenstein and Rothschild, but that annexed, the substance being formed by rupture of the pyridine ring (compare Zincke, Abstr., 1904, i, 921). It is reconverted into the yellow betaine anhydride by hydrogen chloride in glacial acetic acid at 100°, and is decomposed by hot hydrochloric acid, yielding 4 : 6-dinitro-3-aminophenol, and by hot aniline, yielding the dinitroaminophenol and the dianilide, NPh:CH·CH:CH·CH:CH·NHPh, previously described.



Dinitrophenyldipyridinium dichloride forms colourless prisms containing $2H_2O$, which decompose by heating, pyridine, hydrogen chloride, and the yellow anhydride being produced. An aqueous solution, by treatment with sodium carbonate, or, better, with ammonium hydroxide, becomes violet, and finally deposits a blackish-green precipitate of a *substance*, $C_{16}H_{14}O_6N_4$, which forms red salts (the *chloride*, *platinichloride*, *bromide*, and *nitrate* are described), and receives the annexed constitution,

one pyridine ring being ruptured and the other converted into the ψ-form. The substance yields the yellow betaine anhydride by treatment with boiling glacial acetic acid and acetic anhydride, and is decomposed by boiling 2*N*-hydrochloric acid, yielding 4 : 6-*dinitro*-3-*aminophenylpyridinium chloride*, $C_{11}H_9O_4N_4Cl$, m. p. 230—235° (decomp.). The blackish-green substance is also decomposed by aniline, yielding dinitrodiaminobenzene and the dianilide mentioned above. C. S.

Quinoline Sulphosalicylate. Georges Prunier (*J. Pharm. Chim.*, 1910, [vii], 1, 538—539).—*Quinoline sulphosalicylate*,

$$HSO_3{\cdot}C_6H_3(OH){\cdot}CO_2H,C_9H_7N,H_2O,$$

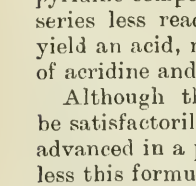
obtained by the action of the acid on the base in presence of water, melts partly at 110° and becomes anhydrous, and then melts at 220°. It crystallises in colourless, silky tufts, is sparingly soluble in cold water (1·547 parts per 100 at 17°), more so in warm water or alcohol, and is acid in reaction. It is poisonous in doses of 0·29 to 0·34 gram per kilogram of body-weight when applied subcutaneously or intravenously. Its antiseptic power is about the same as that of phenol, and its bactericidal action somewhat less. Its reactions with a number of common reagents are tabulated. T. A. H.

Ketens. II. Dimethylketen Bases. Hermann Staudinger, Helmut W. Klever, and P. Kober (*Annalen*, 1910, **374**, 1—39. Compare Abstr., 1907, i, 424; 1908, i, 318).—An investigation of the keten bases formed by the combination of dimethylketen with tertiary bases.

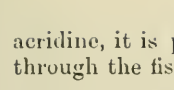
The dimethylketen bases, as a general rule, when treated with dilute mineral acids or alkalis, unite with a molecule of water, yielding acids having the composition 1 mol. base + 1 mol. keten + 1 mol. water or 1 mol. base + 1 mol. keten + 1 mol. *iso*butyric acid respectively. The corresponding esters and anilides of the acids may be obtained by acting on the keten base with an alcohol or aniline. The acids are converted by hot strong mineral acids into 2 mols. of *iso*butyric acid and 1 mol. of the tertiary base, and decompose when heated at a high temperature; for example, dimethylketenquinoline decomposes into quinoline and *iso*butyric anhydride.

The reactivities of the dimethyl-keten bases and of the acids derived from them varies with the nature of the tertiary base; thus, the pyridine compounds are very unstable, the derivatives of the quinoline series less reactive, whilst keten-acridine is so stable that it does not yield an acid, neither is it possible to decompose it with the formation of acridine and *iso*butyric acid.

Although the several reactions of dimethylketenquinoline may be satisfactorily accounted for by means of the constitutional formula advanced in a previous paper (compare Abstr., 1907, i, 424), nevertheless this formula is shown to be incorrect and must be replaced by the annexed formula, for it is found that Schiff's bases combine with 2 mols. of keten, the combination taking place through the C:N– linking. It is for this reason that only tertiary bases containing the C:N– group combine with dimethylketen; in the case of

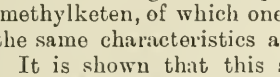


acridine, it is probable that the formation of the keten base results through the fission of the para-linking, the base having the annexed formula. Generally speaking, Schiff's bases combine with dimethylketen, yielding β-lactams, which undergo further change into β-amino-acids; benzylidenebenzylamine, however, in addition to the normal β-lactam, yields two other substances having the composition 1 mol. of Schiff's base + 2 mols. of dimethylketen, of which one, the chief product of the reaction, possesses the same characteristics as the dimethylketen bases already discussed. It is shown that this substance is 2 : 4-diketo-6-phenyl-1-benzyl-3 : 3 : 5 : 5-tetramethylpiperidine, since the acid formed by the action of a dilute solution of sodium carbonate on the keten base is identical with the substance obtained by treating the corresponding ester of β-benzylamino-β-phenyl-$\alpha\alpha$-dimethylpropionic acid with *iso*butyric anhydride.



Benzylidenemethylamine, in analogy to benzylidenebenzylamine, reacts with dimethylketen, yielding as chief product a keten base.

Dimethylketenquinoline (compare Abstr., 1907, i, 424), when heated with dilute hydrochloric acid on a water-bath, yields an *acid*,

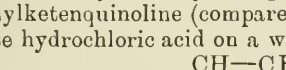


which forms colourless, compact crystals, m. p. 152—153°; many derivatives of the acid have been described previously (*loc. cit.*).

Dimethylketen-β-naphthaquinoline, $C_{21}H_{21}O_2N$, forms white crystals, m. p. 163°; the *acid* derived from it, $C_{21}H_{23}O_3N$, crystallises in white needles, m. p. 171°.

*Dimethylketen**iso**quinoline*, $C_{17}H_{19}O_2N$, crystallises in leaflets and needles, m. p. 105°; it gives rise to an *acid*, $C_{17}H_{21}O_3N$, which forms white crystals, m. p. 138°. The *acid*, $C_{13}H_{19}O_3N$, derived from dimethylketenpyridine, crystallises in large, colourless, prisms, m. p. 94—95°.

2 : 4-*Diketo*-6-*phenyl*-1-*benzyl*-3 : 3 : 5 : 5-*tetramethylpiperidine*,



prepared from dimethylketen and benzylidenebenzylamine, could not be isolated in a pure state; it is converted by a hot aqueous solution of sodium carbonate chiefly into β-iso*butyrylbenzylamino*-β-*phenyl*-$\alpha\alpha$-*dimethylpropionic acid*, $CHMe_2\cdot CO\cdot N(CH_2Ph)\cdot CHPh\cdot CMe_2\cdot CO_2H$, which forms colourless crystals, m. p. 169·5° (decomp.); the *silver* salt is a crystalline, white powder. The acid is decomposed by boiling concentrated hydrochloric acid, yielding benzylamine, β-benzylamino-β-phenyl-$\alpha\alpha$-dimethylpropionic acid, *iso*butyric acid, benzaldehyde, dimethylstyrene, and *benzylbutyramide*, $C_{11}H_{15}ON$, white leaflets, m. p. 92°. Oxidation of the acid by potassium permanganate leads to the formation of *iso*butyric acid, benzoic acid, and a *substance*, $C_{22}H_{25}O_3N$, obtained as a white, crystalline powder, m. p. 195°. The following derivatives of the acid were prepared either from the acid or from the keten base by the usual methods: *methyl* ester, $C_{23}H_{29}O_3N$, large, colourless prisms, m. p. 109°; *ethyl* ester, $C_{24}H_{31}O_3N$, m. p. 111—112°; *bromide*, an amorphous powder which could not be

purified; *anilide*, $C_{28}H_{32}O_2N_2$, a white, crystalline powder, m. p. 138°; *phenylhydrazide*, $C_{28}H_{33}O_2N_3$, colourless, felted needles, m. p. 155°.

The *lactam* of *β-benzylamino-β-phenyl-αα-dimethylpropionic acid*, $CMe_2<^{CHPh}_{CO--}>N\cdot CH_2Ph$, is formed, together with *iso*butyric acid, by heating the acid just described at 180°; it forms large, white prisms, m. p. 36°, and is not altered by a hot alcoholic solution of phenylhydrazine or hydroxylamine, but is converted by an alcoholic solution of potassium hydroxide into the salt of the corresponding acid; the solution of the potassium salt thus obtained, when acidified with acids, yields the corresponding salts; the *acetate*, $C_{18}H_{21}O_2N,Me\cdot CO_2H$, is a white, crystalline powder, m. p. 190—191° (decomp.); the *hydrochloride*, $C_{18}H_{21}O_2N,HCl$, forms crystalline nodules, m. p. 142°. The *amino-acid* is obtained by dissolving the acetate in a known excess of aqueous sodium hydroxide, and adding the requisite quantity of hydrochloric acid; it crystallises with $1H_2O$ in small, white needles, m. p. 138—142°; the anhydrous substance has m. p. 145—148°; the *ethyl* ester, $C_{20}H_{25}O_2N$, prepared from the silver salt and ethyl iodide, has m. p. 63—64°. Attempts to replace the hydrogen of the NH-group by the *iso*butyryl group by heating the acid with *iso*butyryl chloride led to the formation of the *β*-lactam. The *iso*butyryl group can be introduced, however, by heating the ethyl ester with *iso*butyric anhydride.

The formation of 2 : 4-diketo-6-phenyl-1-benzyl-3 : 3 : 5 : 5-tetramethylpiperidine from dimethylketen and benzylidenebenzylamine is accompanied by the formation of the *β*-lactam just described, together with a *substance*, $C_{22}H_{25}O_2N$, m. p. 117°, which is extremely stable towards acids and alkalis.

Dimethylketen-benzylidenemethylamine, *2 : 4-diketo-6-phenyl-1 : 3 : 3 : 5 : 5-pentamethylpiperidine*, prepared from dimethylketen and benzylidenemethylamine, could not be obtained pure; when heated with an aqueous solution of sodium carbonate, it yields the corresponding *acid*, $C_{16}H_{23}O_3N$, a white, crystalline powder, m. p. 142° with evolution of *iso*butyric acid; the *methyl* ester, $C_{17}H_{25}O_3N$, crystallises in white needles, m. p. 78°. The acid, when heated at 150°, yields the *lactam* of *β-methylamino-β-phenyl-αα-dimethylpropionic acid*, $C_{12}H_{15}ON$, an oil, b. p. 139·5°/13 mm.; the corresponding *acid*, $C_{12}H_{17}O_2N$, is obtained as a crystalline powder, m. p. 260°, which is possibly an internal ammonium salt. A *substance*, $C_{16}H_{21}O_3N$, is formed as a by-product in the interaction of dimethylketen and benzylidenemethylamine; it forms crystals, m. p. 115°. W. H. G.

Researches on Benzidine Formation. Henri Duval (*Bull. Soc. chim.*, 1910, [iv], **7**, 527—538).—A résumé of results already published, in part, in Abstr., 1905, i, 651; 1906, i, 314; 1909, i, 747. The following new compounds are described: *2 : 2′-Dinitro-4 : 4′-diacetylaminodiphenylmethane*, $CH_2[C_6H_3(NO_2)\cdot NH_2]_2$, m. p. 229°, forms yellow crystals, and on reduction with stannous chloride yields the corresponding *2 : 2′-diamino*-compound, m. p. 244°, which crystallises in colourless needles from dilute alcohol.

4 : 4′-Tetramethyldiamino-2 : 2′-azodiphenylmethane, on reduction

with stannous chloride in hydrochloric acid, furnishes 4 : 4′-tetramethyldiamino-2 : 2′-diaminodiphenylmethane (Pinnow, Abstr., 1895, i, 98), and this on further reduction with zinc dust and sodium hydroxide gives 4 : 4′-tetramethyldiaminoacridine (Biehringer, Abstr., 1897, i, 73). T. A. H.

Action of Hypochlorous Acid and of Sodium Hypochlorite on Hydantoin and Acetylenediureine. Heinrich Biltz and Otto Behrens (*Ber.*, 1910, 43, 1984—1996. Compare Abstr., 1909, i, 848).—Sodium hypochlorite reacts with hydantoins and acetylenediureines, so that the H of one NH-group becomes replaced by Cl, and that of the second NH-group by Na; thus diphenylhydantoin yields $\begin{matrix}CPh_2\cdot NCl\\ |\\ CO-NNa\end{matrix}>CO$. If, however, an excess of free hypochlorous acid is used, both hydrogens are replaced by chlorine, and a compound of the type $\begin{matrix}CPh_2\cdot NCl\\ |\\ CO-NCl\end{matrix}>CO$ is formed. The chlorides can be crystallised from chloroform, but react readily with hydroxyl compounds, for example, with ethyl alcohol the original hydantoin is formed, together with acetaldehyde and chlorine. They also react readily with an aqueous solution of potassium iodide liberating iodine; the reaction proceeds in the two stages: (1) $>NCl + H_2O \rightleftarrows >NH + HOCl$; (2) $HOCl + 2HI = HCl + H_2O + I_2$. All the chlorides obtained are colourless and odourless, like most *N*-halide derivatives of acylamines, whereas *N*-halogenated alkylamines have pungent odours.

1 : 3-*Dichloro*-5 : 5-*diphenylhydantoin*, $\begin{matrix}CPh_2\cdot NCl\\ |\\ CO-NCl\end{matrix}>CO$, crystallises in well-developed, six-sided prisms, m. p. 164° (decomp.). It crystallises from benzene with $\frac{1}{2}C_6H_6$, which it loses at 108°. When methylated by means of methyl sulphate and dilute alkali, it yields 5 : 5-diphenyl-1 : 3-dimethylhydantoin (Biltz and Rimpel, Abstr., 1908, i, 462). 1-*Chloro*-5 : 5-*diphenyl*-3-*methylhydantoin*, $\begin{matrix}CPh_2\cdot NCl\\ |\\ CO-NMe\end{matrix}>CO$, prepared by the action of sodium hypochlorite on 5 : 5-diphenyl-3-methylhydantoin, crystallises in prisms, m. p. 186° (decomp.). 1 : 3-*Dichloro*-5 : 5-*dibromophenylhydantoin*, $\begin{matrix}(C_6H_4Br)_2C-NCl\\ |\\ CO\cdot NCl\end{matrix}>CO$, crystallises in rhombic plates, m. p. 241° (decomp.), and can be readily methylated, and yields the same 5 : 5-*dibromophenyl*-1 : 3-*dimethylhydantoin*, $C_{17}H_{14}O_2N_2Br_2$, m. p. 199°, as is obtained by methylating di-5-bromophenylhydantoin itself, or by condensing dibromobenzil with dimethylcarbamide at 210°.

4 : 5-*Dibromophenyl*-1 : 3-*dimethylglyoxalone*-4 : 5-*glycol*, $\begin{matrix}C_6H_4Br\cdot C(OH)\cdot NMe\\ |\\ C_6H_4Br\cdot C(OH)\cdot NMe\end{matrix}>CO$, obtained by boiling a mixture of dibromobenzil and *s*-dimethylcarbamide with sodium ethoxide solution for two hours, crystallises in rhombic plates, m. p. 212°. When heated at its m. p., it loses water and yields 5 : 5-dibromophenyl-1 : 3-dimethylhydantoin.

5 : 5-*Dibromophenyl*-3-*methylglyoxalone*, $(C_6H_4Br)_2C(NH)\cdot CO\cdot NMe\cdot CO$, is obtained by boiling dibromobenzil and methylcarbamide with an alcoholic solution of sodium ethoxide for three hours, and crystallises in rhombic plates or prisms, m. p. 267°.

1-*Chloro*-5 : 5-*dibromophenylhydantoin*, $(C_6H_4Br)_2C(NCl)\cdot CO\cdot NH\cdot CO$, obtained by the action of carbon dioxide on its sodium derivative, crystallises in compact rhombohedra, m. p. 203° (decomp.). When diphenylthiohydantoin is treated with sodium hypochlorite and then with carbon dioxide, diphenyldichlorohydantoin is obtained.

1 : 3 : 7 : 9-*Tetrachloro*-4 : 5-*diphenylacetylenediureine*,

$$CO<\begin{matrix}NCl\cdot CPh\cdot NCl\\ |\\ NCl\cdot CPh\cdot NCl\end{matrix}>CO,$$

crystallises in six-edged prisms, m. p. 249° (decomp.).

1-*Chloro*-3-*sodium*-4 : 5-*diphenylacetylenediureine*,

$$CO<\begin{matrix}NCl-CPh\cdot NH\\ |\\ NNa\cdot CPh\cdot NH\end{matrix}>CO,$$

crystallises in long, glistening prisms, and, when carbon dioxide is passed into its aqueous solution, yields 1-*chloro*-4 : 5-*diphenylacetylenediureine*, $C_{16}H_{13}O_2N_4Cl$, which crystallises from acetone in six-sided prisms, m. p. 218° (decomp.).

Acetylenediureine is not so stable towards sodium hypochlorite, and at 95° yields 30% of free nitrogen. 4 : 5-Dimethylacetylenediureine behaves in a similar manner. J. J. S.

Catalytic Racemisation of Optically Active Hydantoin Derivatives and of Related Substances as the Result of Tautomeric Change. Henry D. Dakin (*Amer. Chem. J.*, 1910, **44**, 48—60).—In *N*-sodium hydroxide the rotation of the active hydantoins,

$$CHR<\begin{matrix}NH\cdot CO\\ |\\ CO-NH\end{matrix}$$

(where R is $\cdot CH_2Pr^{\beta}$, *p*-$OH\cdot C_6H_4\cdot CH_2$, $\cdot CH_2\cdot CO_2H$, or $\cdot CH_2\cdot CH_2\cdot CO_2H$),

diminishes to zero in the course of many hours, the solutions then yielding the *i*-hydantoins by acidification. The rotation of the corresponding carbamido-acids remains constant in *N*-sodium hydroxide. The loss of activity of the hydantoins is most obviously explicable by enol-keto-desmotropy, $CH\cdot CO \rightleftharpoons C(OH)\cdot CO$ (compare Wren, Trans., 1909, **95**, 1593), the correctness of the explanation being supported by the case of the hydantoin, $CMeEt<\begin{matrix}NH\cdot CO\\ |\\ CO-NH\end{matrix}$, obtained from *iso*valine, the rotation of which remains constant in *N*-sodium hydroxide.

The following new compounds have been obtained by evaporating active *α*-amino-acids with aqueous potassium cyanate, and boiling the resulting active hydantoic acids with 10% hydrochloric acid: d-iso-*Butylhydantoic acid*, m. p. 205—206° (decomp.), $[\alpha]_D^{20}$ 1·9° in *N*-sodium hydroxide ($c = 3{\cdot}15$), from *l*-leucine; l-iso*butylhydantoin*, m. p. 212°,

$[\alpha]_D^{20}$ $-68{\cdot}2°$ in *N*-sodium hydroxide ($c = 1{\cdot}925$), becoming 0 after thirty hours; d-*methylethylhydantoin*, m. p. 172—173°, $[\alpha]_D^{20}$ 32° ($c = 1{\cdot}247$), from *l-iso*valine. C. S.

Two Isomeric Benzylglyoxalidones. Hermann Finger and W. Zeh (*J. pr. Chem.*, 1910, [ii], 82, 50—60).—Two isomeric benzylglyoxalidones are obtained when benzyliminoethyl ether is employed in the reaction described previously (Abstr., 1906, i, 901; 1907, i, 876). 4-*Keto*-2-*benzyl*-4 : 5-*dihydroglyoxaline*,

$$CH_2Ph\cdot C\lessdot \begin{matrix} N{-}{-}CO \\ | \\ NH\cdot CH_2 \end{matrix}',$$

m. p. 143°, obtained by keeping the imino-ether and ethyl glycine at 20° for two hours, is a weak monoacidic base. It is decomposed by hydrochloric acid, D 1·12, at 130° into phenylacetic acid, glycine, and ammonia, reacts with boiling water to form a *substance*,

$$C_{10}H_{12}O_2N_2,$$

m. p. 176—177°, which is probably phenylacetylglycinamide, forms with *p*-nitrodiazobenzene chloride in the presence of sodium acetate 5-p-*nitrobenzeneazo*-2-*benzylglyoxalidone*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot CH\lessdot \begin{matrix} CO{-}{-}N \\ \| \\ NH\cdot C\cdot CH_2Ph \end{matrix}',$$

yellow needles, darkening at 235°, combines with phenylcarbimide to form a *phenylcarbamide*, $C_{17}H_{15}O_2N_3$, with phenylthiocarbimide to form a *phenylthiocarbamide*, $C_{17}H_{15}ON_3S$, yields a *dibenzoyl* derivative,

$$CH_2Ph\cdot C\lessdot \begin{matrix} N{-}{-}COBz \\ | \\ NBz\cdot CH \end{matrix}',$$

m. p. 138°, with benzoyl chloride in pyridine, *benziminylbenzylglyoxalidone*, $NH{:}CPh\cdot N\lessdot \begin{matrix} CH_2{-}{-}{-}{-}CO \\ | \\ C(CH_2Ph){:}N \end{matrix}$, sulphur-yellow leaflets, m. p. 237°, with benziminoethyl ether, 5-*benzyl*-2-*benzylideneglyoxalidone*, m. p. 177·5°, with benzaldehyde in faintly alkaline solution, condenses with diacetyl to form a reddish-orange *substance*, $C_{14}H_{14}O_2N_2$, decomposing at 196°, and reacts with isatin in hot glacial acetic acid to form a scarlet indigoid *dye*,

$$NH\lessdot \begin{matrix} CO \\ | \\ C_6H_4 \end{matrix}\gtrdot C{:}C\lessdot \begin{matrix} CO{-}N \\ \| \\ NH\cdot C\cdot CH_2Ph \end{matrix}'$$

which is reduced by alkaline hyposulphite to a yellowish vat-dye, oxidising rapidly in air.

The isomeric substance, iso*benzylglyoxalidone*, $C_{13}H_{10}O_2N_2$, m. p. 222° (decomp.), which is the chief product of the reaction when benzyliminoethyl ether and ethyl glycine are heated together, is probably the cyclic amidine, $CH_2Ph\cdot C\lessdot \begin{matrix} N{-}{-}CH_2 \\ | \\ NH\cdot CO \end{matrix}$. It is not attacked by boiling water, yields phenylacetic acid, glycine, and ammonia when decomposed by hydrochloric acid at 140°, forms an *acetyl* derivative, m. p. 189° (not sharp), with acetic anhydride, gives successively yellow, greenish-blue, reddish-violet, and red colorations when heated with glacial acetic acid, and yields a *substance*, $C_{18}H_{16}O_2N_2$, by heating with sodium hydroxide and subsequent acidification.

C. S.

Decomposition of Indigotin and of Indirubin by Alkalis. Paul Friedländer and Erw. Schwenk (*Ber.*, 1910, **43**, 1971—1975. Compare Fritzsche, *Annalen*, 1841, **39**, 79; Heumann and Bachofen, Abstr., 1893, i, 270; Hentschel, *ibid.*, 1900, i, 231).—The decomposition of indigotin by alkalis cannot take place according to the equation given by Henschel, as the amount of indoxyl is very small, and varies with the temperature and the length of time of heating. The indoxyl is a secondary decomposition product. Fritzsche's chrysanilic acid is not a primary decomposition product; it is formed by the condensing action of the added acid on anthranilic acid and indoxyl-2-aldehyde, both of which are present as potassium salts after the fusion. The two are separated by taking the dilute solution of the fused mass, freeing it from indoxyl, and pouring into cold dilute hydrochloric acid, which is continually stirred, and also covered with a layer of ether. The anthranilic acid is then present in the aqueous, and the aldehyde in the ethereal, solution.

Indoxyl-2-aldehyde, $C_6H_4\langle^{C(OH)}_{NH}\rangle C\cdot CHO$, crystallises from warm water or from a mixture of chloroform and light petroleum in glistening needles, which decompose at about 160°. It condenses with anthranilic acid in the presence of acids, yielding chrysanilic acid,

$$CO_2H\cdot C_6H_4\cdot N:CH\cdot C\langle^{C(OH)}_{NH}\rangle C_6H_4.$$

The decomposition of indigotin may be represented by the scheme:

$$C_6H_4\langle^{CO}_{NH}\rangle C:C\langle^{CO}_{NH}\rangle C_6H_4 \longrightarrow$$

$$C_6H_4\langle^{CO}_{NH}\rangle C(OH)\cdot C\langle^{C(ONa)}_{NH}\rangle C_6H_4 \longrightarrow$$

$$NH_2\cdot C_6H_4\cdot CO_2H + C_6H_4\langle^{C(OH)}_{NH}\rangle C\cdot CHO.$$

When indirubin is heated with concentrated sodium hydroxide at 150°, it is transformed into a sparingly soluble *sodium* salt,

$$C_{16}H_{11}O_2N_2Na,$$

from which acids liberate the *acid*, $C_{16}H_{12}O_3N_2$. This crystallises from nitrobenzene in long, glistening, yellow needles, m. p. above 295°. When heated at 150°, it yields carbon dioxide, aniline, and oxindole, and as it can be synthesised from anthranilic acid and oxindole-3-aldehyde, is represented as

$$CO_2H\cdot C_6H_4\cdot N:CH\cdot C\langle^{C(OH)}_{C_6H_4}\rangle NH.$$

The action of alkali on indirubin is thus analogous to its action on indigotin:

$$C_6H_4\langle^{CO}_{NH}\rangle C:C\langle^{CO}_{C_6H_4}\rangle NH \longrightarrow$$

$$C_6H_4\langle^{CO}_{NH}\rangle C(OH)\cdot C\langle^{C(ONa)}_{C_6H_4}\rangle NH \longrightarrow$$

$$CO_2H\cdot C_6H_4\cdot N:CH\cdot C\langle^{C(OH)}_{C_6H_4}\rangle NH.$$

Oxindole-3-aldehyde, $C_6H_4\langle^{C(CHO)}_{NH}\rangle C\cdot OH$, is prepared readily by the action of alkalis on thioindigo-scarlet (3′-indoxyl-2-thionaphthen-

3-one: Bezdzik and Friedländer, Abstr., 1908, i, 673), the other product being *o*-thiolbenzoic acid. The aldehyde crystallises from dilute alcohol in pale yellow needles, m. p. 213°, and is more stable than indoxyl-2-aldehyde. J. J. S.

Condition of Indigo-White in Aqueous Solutions. Edmund Knecht and J. P. Batey (*J. Soc. Dyers*, 1910, 28, 171—173).—Calcium indigo-white has been shown by the boiling-point method to be crystalloid in solution. A solution of purified monosodium indigo-white is found to be an electrolyte. The material was prepared by mixing alcoholic sodium hydroxide with an excess of alcoholic indigo-white in an atmosphere of hydrogen, evaporating to dryness, and treating the residue with air-free water for two and a-half hours. The indigo-white in the solution, determined by oxidation and direct weighing, was very slightly in excess of the proportion required for pure monosodium salt.

The molecular conductivity of monosodium indigo-white is 62·6 at 19·35 litres and 67·7 at 37·85 litres dilution, that is, about 2/3 the conductivity of sodium chloride.

Cotton adsorbs indigo-white and sodium hydroxide in approximately equivalent proportions from a solution of monosodium salt, but more indigo and more alkali are adsorbed in presence of excess of sodium hydroxide. No definite relation between the amounts of indigo and alkali taken up in these cases could be found, but as nearly all the indigo can be washed out with air-free water, the action is doubtless an adsorption by the cotton. R. J. C.

Condensation of Phenyl*iso*oxazolone with Ethyl Mesoxalate. André Meyer (*Compt. rend.*, 1910, 150, 1765—1767. Compare Abstr., 1908, i, 368).—When an alcoholic solution of ethyl mesoxalate (1·1 mol.) is boiled for thirty minutes with phenyl*iso*oxazolone, a good yield of *ethyl bisphenyl*iso*oxazolonemesoxalate*,

$$C(CO_2Et)_2\left(CH<\begin{matrix}CO-O\\ |\\ CPh:N\end{matrix}\right)_2,$$

is obtained. This compound crystallises in large octahedra, m. p. 187° (decomp.), and forms solutions in aqueous alkali hydroxides or carbonates, from which it is precipitated by the addition of mineral acids. The *sodium* salt, $C_{25}H_{20}O_8N_2Na_2$, occurs in hexagonal crystals; its aqueous solution gives a violet precipitate with ferric chloride; the *silver*, *lead*, *mercuric*, and *zinc* salts are insoluble. The *diethyl* derivative, $C_{29}H_{30}O_8N_2$, obtained by the action of ethyl iodide on the sodium salt, crystallises in slender needles, m. p. 200—201°. The *diacetyl* derivative forms prisms, m. p. 166°; the *dibenzoyl* derivative has m. p. 194°.

The addition of benzenediazonium chloride to a solution of the compound in alkali results in the formation of Claisen's benzeneazophenyl-*iso*oxazolone (Abstr., 1891, 468). W. O. W.

Action of Hydrazoic Acid on Some Acids of the Acetylene Series. Synthesis of Derivatives of 1 : 2 : 3-Triazole. E. Oliveri-Mandalà and A. Coppola (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 563—569. Compare Oliveri, *ibid.*, 1905, [v], 14, i, 228).—When an

ethereal solution of acetylenedicarboxylic acid (Perkin, Trans., 1907, 91, 834) is warmed for a short time with an ethereal solution of hydrazoic acid, 1 : 2 : 3-triazoledicarboxylic acid, identical with that of Bladin and of Zincke (Abstr., 1896, i, 550), is obtained. This substance yields with 3 molecules of diazomethane a *trimethyl* derivative, m. p. 55—60°, in which one of the methyl groups is attached to nitrogen, since it yields methylamine when boiled with concentrated alkali. Phenylpropiolic acid and hydrazoic acid react but slowly, only 7/10 of the substances having condensed after six days at 45—50°. The behaviour of this acid with hydrochloric acid is similar (Michael and Pendleton, Abstr., 1889, 1063). The product, 4-*phenyl*-1 : 2 : 3-*triazole*-5-*carboxylic acid*, has m. p. 205—206°, decomposing into carbon dioxide and phenyltriazole. Analysis indicated the presence of $\frac{1}{2}H_2O$, but it was not possible to eliminate this from the substance. The *barium* salt crystallises with $2H_2O$. 4-*Phenyl*-1 : 2 : 3-*triazole*, obtained by heating the above acid at 210—215°, has m. p. 143—145°, and displays both basic and acid properties; it yields a *silver* salt, dissolves in dilute alkalis, and is precipitated again by acids; it forms a *hydrochloride*, m. p. about 140°, and a *platinichloride*. 1 : 2 : 3-Triazolecarboxylic acid (Dimroth, Abstr., 1902, i, 403) can be prepared similarly. R. V. S.

Decomposition of Certain Cyclic Imines by means of Sodium Hypochlorite Heinrich Biltz and Otto Behrens (*Ber.*, 1910, 43, 1996—1999).—Allantoin, 3-methylallantoin, 5-hydroxy-1 : 3-dimethylhydantoylcarbamide (Biltz, this vol., i, 521), 7 : 9-dimethyluric acid glycol, and parabanic acid give almost theoretical amounts of nitrogen at the ordinary temperature in the presence of sodium hypochlorite solution and excess of potassium hydroxide. Uric acid and its methyl derivatives under similar conditions evolve nitrogen slowly, and in most cases the amount of nitrogen corresponds with the non-methylated imino-groups present. An exception is 7-methyluric acid.

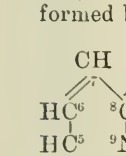
Alloxan also reacts but slowly with hypochlorite. Methyl- and dimethyl-carbamides react only slowly with hypochlorite. J. J. S.

Methylation and Constitution of Allantoin. Heinrich Biltz (*Ber.*, 1910, 43, 1999—2003. Compare Siemonsen, Abstr., 1904, i, 951).—3-Methylallantoin can be prepared by the action of methyl iodide on the silver salt of allantoin. Although the yield is only 33% of the theoretical, this is probably the most convenient method for the preparation for the 3-methyl derivative. 3-Methylallantoin is not reduced so readily as allantoin, and after treatment with 1% sodium amalgam in slightly acid solution, yields carbamide, 3-methylhydantoin, and unaltered substance.

The behaviour of allantoin towards sodium hypochlorite, namely, the elimination of two of the four atoms of nitrogen, is in harmony with Grimaux's formula, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH<\begin{matrix}NH{\cdot}CO\\ |\\ CO{-}NH\end{matrix}$. The alternative formula, hydroxyacetylenediureine, $CO<\begin{matrix}NH{\cdot}CH{-}{-}{-}NH\\ |\\ NH{\cdot}C(OH){\cdot}NH\end{matrix}>CO$, cannot

be correct, as such a compound should be stable towards hypochlorite; further, allantoin gives none of the reactions characteristic of hydroxy-compounds. J. J. S.

Heterohydroxylic Acids. Carl Bülow and Carl Haas (*Ber.*, 1910, i, 43, 1975—1984. Compare Abstr., 1909, i, 613—616; this vol., i, 80—81).—As heterohydroxylic acids are denoted the compounds formed by the condensation of 1-amino-1 : 3 : 4-triazole with the esters of γ-carboxylic acids. The hydroxylic group in position 7 (annexed formula of 1 : 2 : 4 : 9-benztetrazole) imparts pronounced acid properties to the compounds, so that they can be titrated readily with standard sodium hydroxide. A comparison of these hydroxylic acid compounds with ordinary carboxylic acid has been made. Their esters cannot be prepared by the ordinary catalytic method of esterification, by the action of alcohol on the corresponding chloride, or by the action of methyl sulphate on the alkali salts, but are formed when the silver salts are treated with alkyl iodides. They can be benzoylated by the Schotten-Baumann process, but the resulting benzoates are hydrolysed readily by dilute alkalis. A mixture of phosphorus pentachloride and oxychloride transforms the hydroxy-compounds into the corresponding chlorides, which are much more stable than ordinary acyl chlorides; they can be crystallised from alcohol or water, but react readily with potassium hydrogen sulphide, yielding thiols, which are readily oxidisable compounds with pronounced acidic properties. The chlorides form salts with strong acids, but these are fairly readily hydrolysed. The hetero-condensed, heterocyclic system is stable towards concentrated hydrochloric acid, and the acids may be heated with the hydrochloric acid at 140° without appreciable decomposition; but they are readily decomposed when fused with potash at 280°, one of the products being hydrogen cyanide.



7-Hydroxy-5-methyl-1 : 2 : 4 : 9-benztetrazole (compare Abstr., 1909, i, 615) is best prepared by heating 1-amino-1 : 3 : 4-triazole (11 grams) with ethyl acetoacetate (19 grams), first at 130°, then for one hour at 150°, and finally at 160—170° for a quarter to half an hour. The *sodium* salt, $C_6H_5ON_4Na$, crystallises from alcohol in colourless needles; the *ethyl* ester, $C_8H_{10}ON_4$, crystallises from a mixture of benzene and light petroleum, and has m. p. 170—171°; the *benzoate*, $C_{13}H_{10}O_2N_4$, crystallises from methyl alcohol in long prisms containing methyl alcohol, or from ethyl acetate in cubes, m. p. 157—158°. *7-Chloro-5-methyl-1 : 2 : 4 : 9-benztetrazole*, $C_6H_5N_4Cl$, crystallises in long, yellow, glistening needles, m. p. 185°; the corresponding *iodide*, $C_6H_5N_4I$, crystallises in large, colourless needles, m. p. 211—212°, and forms a *hydriodide*, m. p. 196—197°, which is obtained when the hydroxy-compound is boiled for six hours with concentrated hydriodic acid and red phosphorus.

5-Methyl-1 : 2 : 4 : 9-benztetrazole-7-thiol,

$$\begin{matrix} CMe{:}N & \text{---} & N{\cdot}CH \\ | & & | \\ CH{:}C(SH){\cdot}C & = & N \end{matrix} \gg N,3H_2O,$$

crystallises in long, yellow needles, sinters at 150°, but is not com-

pletely molten at 280°; its aqueous solution when boiled in contact with the air yields a brown, amorphous, flocculent mass.

When the chloride is reduced with zinc dust and water, 5-*methyl*-1 : 2 : 4 : 9-*benztetrazole*, $\begin{matrix}\mathrm{CMe{:}N{\cdot}N{\cdot}CH}\\ \mathrm{CH{:}CH{\cdot}C{=}N}\end{matrix}\!\!>\!\mathrm{N}$, is formed, and can be isolated as the *picrate*, $C_6H_6N_4,C_6H_3O_7N_3$, which crystallises in yellow cubes, m. p. 162—163°. The base crystallises in colourless needles, m. p. 158—159°.

When the hydroxy-compound is heated with five times its weight of phenylhydrazine, it yields 4-anilinoazo-1-phenyl-3-methyl-5-pyrazolone (this vol., i, 233) together with other products. The hydroxy-compound reacts with hydrazine, yielding a *salt*, $C_6H_6ON_4,N_2H_4$, which crystallises from alcohol in large, glistening plates. J. J. S.

Reduction of Nitro-compounds with Zinc Dust and Acetic Acid. III. Gustav Heller (*Ber.*, 1910, 43, 1907—1922. Compare Abstr., 1908, i, 867, 913).—[With Edmund Weidner]—The reduction of *o*-nitrobenzamide by zinc dust and 50% acetic acid leads to the formation of small quantities of o-*azoxybenzamide*, m. p. 242° (decomp.), and o-*azobenzamide*, m. p. 284—294° (decomp.), the chief product, however, being benz*iso*oxazolone, which from this method of formation might have the constitution

$$\text{I. } C_6H_4\!<\!\begin{matrix}\mathrm{N(OH)}\\ \mathrm{CO}\end{matrix} \quad \text{or} \quad \text{II. } C_6H_4\!<\!\begin{matrix}\mathrm{NH}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{O}.$$

The first formula harmonises with the amphoteric character of the substance and with the formation of acetyl, benzoyl, and methyl derivatives, but since Reissert's 1-acetoxyoxindole (Abstr., 1909, i, 51), an undoubted *N*-hydroxy-derivative, is reduced to oxindole by zinc dust and 50% acetic acid, whilst 2-acetylbenz*iso*oxazolone is reduced to acetylanthranilic acid, there is no alternative but to accept formula II for benz*iso*oxazolone, a conclusion to which Bamberger and Pyman have arrived at on other grounds (Abstr., 1909, i, 573). *o*-Azobenzamide, when treated with cold concentrated sulphuric acid and sodium nitrite and subsequently heated, yields *benzamide-o-azobenzoic acid*,

$$\mathrm{NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}CO_2H},$$

m. p. 215° (decomp.), and is reduced by glacial acetic acid and zinc dust to o-*hydrazobenzamide*, $N_2H_2(C_6H_4{\cdot}CO{\cdot}NH_2)_2$, m. p. 233°.

The reduction of ethyl *o*-nitrobenzoate by acetic acid and zinc dust yields only ethyl *o*-azoxybenzoate. The reduction of *o*-nitrobenzyl alcohol by zinc dust and 50% acetic acid at 0° and subsequently at 40° yields *o*-azoxybenzyl alcohol and *o*-azobenzyl alcohol.

[With Walter Tischner].—*o*-Nitrophenyl-lactaldehyde is reduced to quinoline by zinc dust, glacial acetic acid, and its own weight of water. *o*-Nitrobenzaldehydediethylacetal is reduced to anthranil, and *β-o*-nitrophenyl-*α*-methyl-lactaldehyde, prepared from *o*-nitrobenzaldehyde and propaldehyde, is reduced in a similar manner to 2-methylquinoline, the *hydrochloride*, C_9NH_6Me,HCl, of which has m. p. 228—230°, and the *mercurichloride*, $3C_9NH_6Me,HCl,2HgCl_2$, m. p. 164—165°.

The reduction of *o*-nitrocinnamic acid by zinc dust and acetic acid in the presence of sodium acetate and water at 40—45° yields about 10%

of *o-azoxycinnamic acid*, m. p. 218° (decomp.), and 50% of *o*-aminocinnamic acid. An aqueous solution of the hydrochloride of the latter and acetic anhydride yields *o-acetylaminocinnamic acid*, m. p. 248—249° (decomp.), which forms carbostyril when heated, and by warming for one hour with acetic anhydride produces *bis*-o : o-*diacetylaminocinnamic anhydride*, $(NAc_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CO)_2O$, m. p. 156—157°. o-*Diacetylaminocinnamic acid*, obtained by heating the anhydride with aqueous sodium acetate and a little acetic acid, has m. p. 158°.

Dibromo-*o*-nitrophenylpropionic acid is readily reduced by zinc dust, glacial acetic acid, and its own weight of water at 0°, yielding *o*-aminocinnamic acid and a little *o*-azoxycinnamic acid. C. S.

Bisazo- and Trisazo-derivatives of Resorcinol. William R. Orndorff and B. J. Ray (*Amer. Chem. J.*, 1910, 44, 1—41).—2 : 4 : 6-*Trisbenzeneazoresorcinol*, m. p. 254°, obtained from diazotised aniline hydrochloride (3 mols.) and resorcinol in sodium hydroxide solution, and also from 4 : 6-bisbenzeneazoresorcinol or from 2 : 4-bisbenzeneazoresorcinol and benzenediazonium chloride (1 mol.) in sodium hydroxide solution, crystallises in yellowish-brown, pleochroic needles, and when boiled with acetic anhydride and sodium acetate forms a *diacetyl* derivative, which separates from its solutions in yellow needles, m. p. 201°, by rapid cooling, or in red, pyramidal crystals, m. p. 203°, by slow cooling, and is reconverted into trisbenzeneazoresorcinol by powdered potassium hydroxide suspended in ether.

Wallach and Fischer's β-bisbenzeneazoresorcinol is shown to be 2 : 4 : 6-trisbenzeneazoresorcinol contaminated with 4 : 6-bisbenzeneazoresorcinol, and, similarly, their β-bis-*p*-tolueneazoresorcinol to be a mixture of 2 : 4 : 6-tris-*p*-tolueneazoresorcinol (the diacetyl derivative crystallises in yellow needles, m. p. 218°, or in red crystals, mutually interconvertible) and 4 : 6-bis-*p*-tolueneazoresorcinol (*diacetyl* derivative, m. p. 198·5°). 2 : 4-*Bis*-p-*tolueneazoresorcinol*, m. p. 230·5°, prepared from diazo-*p*-toluene chloride (2 mols.) and resorcinol in sodium acetate solution, forms a *diacetyl* derivative, m. p. 150°.

2 : 4 : 6-*Tris*-o-*tolueneazoresorcinol*, m. p. 226°, forms a diacetyl derivative, m. p. 176°. 4 : 6-Bis-*o*-tolueneazoresorcinol has m. p. 197° (Wallach gives m. p. 194—195°), and forms a *diacetyl* derivative, m. p. 178°. 2 : 4-*Bis*-o-*tolueneazoresorcinol*, m. p. 212°, prepared like the para-isomeride, forms a *diacetyl* derivative, m. p. 130°.

2 : 4 : 6-*Tris*-α-*naphthaleneazoresorcinol*, m. p. 253° (*diacetyl* derivative, yellow prisms, m. p. 228°, or red, tabular crystals, mutually interconvertible), 2 : 4-*bis*-α-*naphthaleneazoresorcinol*, m. p. 242° (*diacetyl* derivative, m. p. 142°), and *bisbenzeneazo*-p-*diazoaminoazobenzene*, $N(N_2 \cdot C_6H_4 \cdot N_2Ph)_2 \cdot C_6H_4 \cdot N_2 \cdot Ph$, m. p. 184°, are also described; the last-mentioned substance is obtained by adding cold alcoholic aminoazobenzene (3 mols.) and acetic acid (9 mols.) to cold sodium nitrite (2 mols.). C. S.

Heat Coagulation of Proteins. Harriette Chick and Charles J. Martin (*J. Physiol.*, 1910, 40, 404—430).—Crystallised egg-albumin and hæmoglobin were used in the experiments. They are not coagulated by dry heat up to 130°. Heat coagulation is therefore not purely a tem-

perature effect, but a reaction between water and protein. The rate of coagulation of hæmoglobin solutions is proportional to the concentration of the residual hæmoglobin; in the case of egg-albumin, the rate decreases more rapidly than can be accounted for in this way; the crystals are doubtless not homogeneous, and changing conditions are also introduced by the adsorption of acid by the coagulum. Egg-albumin crystals are, as Osborne stated, salts of protein with the acids used in their preparation. Details are given confirmatory of Halliburton's statements as to the effect of acid in hastening the rate of coagulation; it is very considerable. Coagulation of proteins is influenced by temperature in accordance with the law of Arrhenius, but the temperature-coefficient is very high, namely, 1·91 per degree for egg-albumin and 1·3 for hæmoglobin.

It is not correct to speak of proteins having any particular coagulation-temperature. Heat coagulation is a reaction between protein and water, and the effect of temperature is merely to accelerate it. Given constant conditions, however, the method may still be used to differentiate proteins, and even to separate them if two proteins are possessed of different reaction rates. The optimum temperature for enzyme actions is also interpreted in a simple way: two operations are at work, that produced by the enzyme, and the destruction of the enzyme by water. If the influence of the temperature on the latter process is greater than on the former, the effect of the enzyme action is counteracted as the temperature rises, and a point is finally reached when the rate of destruction is so great that the enzyme action is arrested. W. D. H.

Analysis of Proteins. Alexandré Etard and Antony Vila (*Compt. rend.*, 1910, **150**, 1709—1711. Compare Abstr., 1908, i, 584; 1909, i, 124).—After removing diamino-acids from the products of hydrolysis of proteins by the method already described, another group of amino-acids may be precipitated by means of ferrocyanic acid.

W. O. W.

Analysis of Edestin and Zein. Thomas B. Osborne and L. M. Liddle. **Sources of Loss in Analysing the Products of Protein Hydrolysis.** Thomas B. Osborne and D. Breese Jones (*Amer. J. Physiol.*, 1910, **26**, 295—304, 305—328).—A number of incomplete analyses of the two proteins mentioned are described in the first paper. The second paper, as its title indicates, should be studied in detail by those interested in protein analysis. The following table of cleavage products of zein is considered nearer the truth than any previously published.

Glycine	0·00	Tyrosine	3·55
Alanine	9·79	Arginine	1·55
Valine	1·88	Histidine	0·82
Leucine	19·55	Lysine	0·00
Proline	9·04	Tryptophan	0·00
Phenylalanine	6·55	Ammonia	3·64
Aspartic acid	1·71	Carbohydrate	0·00
Glutamic acid	26·17		
Serine	1·02	Total	85·27

W. D. H.

Fibrin-ferment. C. Gessard (*Compt. rend.*, 1910, 150, 1617—1618. Compare Abstr., 1909, ii, 682).—Whilst hæmoglobin is freed from hæmase by a single crystallisation, the operation must be repeated several times to remove the fibrin-ferment. The latter is carried down by calcium phosphate when this is precipitated from a solution of fibrin (obtained by whipping) in physiological salt solution. After washing the calcium phosphate, the fibrin-ferment may be extracted by maceration with horse serum, previously heated for an hour at 60°.

W. O. W.

Behaviour of Hæmoglobin towards Hydrazine and the Question of the Capacity of the Colouring Matter of Blood for Combining with Gases. E. Letsche (*Zeitsch. physiol. Chem.*, 1910, 67, 177—191).—The experiments of Hüfner have been repeated and extended (Abstr., 1889, 426; 1900, i, 267; *Arch. Anat. and Physiol.*, 1894, 156). The spectrophotometric method has been used, and the values of ϵ'/ϵ for hæmoglobin with and without the addition of hydrazine hydrate determined under different conditions. The results show that it is the hydrazine and not some impurity which reacts with the hæmoglobin. The effect of the addition of hydrazine hydrate can also be detected by the naked eye. Methæmoglobin is also affected by hydrazine. Both changes consist partially of reductions, but other reactions take place at the same time.

Hæmoglobin and hæmin solutions behave quite differently towards hydrazine, and the reactions are being subjected to further examination.

The effect of the presence of hydrazine on the solubility of carbonic oxide in hæmoglobin has been studied. Also, the effects of concentration of the hæmoglobin solution and of pressure have been examined (compare Manchot, this vol., ii, 137). Some of the differences found can be explained on the view that the solution of the gas is partly physical, and thus the solubility falls under Henry's Law, but chemical combination also occurs.

J. J. S.

Colouring Matter of Blood. Leon Marchlewski (*Zeitsch. physiol. Chem.*, 1910, 67, 195—196).—Polemical in reply to Küster (this vol., i, 529).

J. J. S.

Oxidation of Pure Oxyhæmoglobin by Hydrogen Peroxide. I. Szreter (*Compt. rend.*, 1910, 151, 97—99. Compare Abstr., 1909, i, 620).—Hydrogen peroxide acts on oxyhæmoglobin at 37°, bringing about simple addition of oxygen, and converting it into a substance which, after purification by dialysis, was obtained in colourless, brilliant spangles containing 0·98% of iron in organic combination. Before dialysis, the substance was hygroscopic and much less stable.

W. O. W.

Behaviour of *d*-Leucyl-*l*-tryptophan towards Autolytic Ferments. Hans Fischer (*Ber.*, 1910, 43, 1963—1964).—The author confirms his previous statement that *d*-leucyl-*l*-tryptophan is attacked by autolytic ferments, including yeast extract.

Abderhalden and Schuler's seemingly negative results (this vol.,

i, 304) are attributable to the fact that the products of hydrolysis have much the same rotation as the original peptide. J. J. S.

Chondroitinsulphuric Acid. Kura Kondo (*Biochem. Zeitsch.*, 1910, 26, 116—130).—The acid was prepared from the cartilage of the nasal septum of pigs, which was treated first with 2% potassium hydroxide for two days. The alkaline liquid, after filtration, was just acidified with acetic acid, and boiled with barium carbonate; this treatment was continued until the whole of the protein was coagulated, and the liquid, after filtration and concentration, was thrown into three times the volume of glacial acetic acid; after solution of the precipitate thus formed in water and reprecipitation with glacial acetic acid, the free acid thus obtained was neutralised with sodium or potassium hydroxide, the solution concentrated, and the sodium or potassium salt precipitated by the addition of alcohol. The composition of the acid prepared thus corresponded approximately with the formula $C_{15}H_{27}O_{16}NS$. It gave strongly the orcin and phloroglucinol reactions, and yielded furfuraldehyde after treatment with acids. It gave also, but in very small yield, an osazone-like substance, melting at 143°. The salts are lævorotatory. The benzoyl derivatives of the scission products obtained by treatment of the chondroitinsulphuric acid with 2—3% hydrochloric acid were also investigated. The product obtained did not contain more than five benzoyl groups. S. B. S.

Lipoids. X. The Detection of Galactose in Lipoids. Sigmund Fränkel and Kurt Linnert (*Biochem. Zeitsch.*, 1910, 26, 41—43).—The authors isolated the galactose obtained by the hydrolysis of brain lipoids in the form of the α-phenylmethylhydrazone, which melted at 189°. They also isolated the sugar by hydrolysing with sulphuric acid, separating the acid after hydrolysis by barium hydroxide and carbonate, evaporating the filtrate, dissolving the residue from evaporation in methyl alcohol, and then adding ether. After several days, the sugar could be separated in crystalline form. S. B. S.

Lipoids. XII. The Phosphatides of Horse Pancreas. Sigmund Fränkel and Theodor R. Offer (*Biochem. Zeitsch.*, 1910, 26, 53—54).—From hot acetone extract of horse pancreas a crystalline substance separates on cooling, which, after filtering from liquid fats, washing with 90% alcohol, and recrystallising from hot absolute alcohol, melts at 120°. Two grams were obtained from 4½ kilos. of the fresh organ. The analyses corresponded with the formula $C_{72}H_{147}O_{11}N_2P$; the substance is a saturated diaminomonophosphatide. S. B. S.

The Protective Action of Proteins on Enzymes. Leopold Rosenthaler (*Biochem. Zeitsch.*, 1910, 26, 9—13).—The addition of proteins (egg-white) protects enzymes from the deleterious action of acids and bases. This protective action could be demonstrated in the cases of δ-emulsin, diastase and invertin. S. B. S.

The Inactivation of Ferments, and the Formation of Anti-ferments in Presence of Collodium and Other Membranes. Albert E. Porter (*Biochem. Zeitsch.*, 1910, 25, 301—304).—The

investigations included the study of pepsin, trypsin, rennet, steapsin, ptyalin, emulsin, and taka-diastase. All these ferments, with the exception of taka-diastase, lose their activity in presence of collodion membranes, and acquire, with the exception of ptyalin, an antifermentative action. Colloids other than collodion, such as egg-white membranes and gelatin, exert a similar action. S. B. S.

Inversion of Sucrose by Invertase. IV. Influence of Acids and Alkalis on the Activity of Invertase. C. S. Hudson and H. S. Paine (*J. Amer. Chem. Soc.*, 1910, 32, 774—779; *Zeitsch. Ver. deut. Zuckerind.*, 1910, 634—641. Compare Abstr., 1908, i, 605, 856; 1909, i, 554).—The work described in this paper was undertaken with the object of determining the conditions of acidity and alkalinity which render invertase inactive, and also those which cause its total destruction.

It has been found that acids and alkalis in small concentrations influence the activity of invertase, whilst in large concentrations they cause its destruction. The destruction by acid at 30° proceeds at a scarcely appreciable rate at a concentration of 0·01*N*, and increases rapidly with the acidity until it becomes almost instantaneous at 0·05*N*. The rate of destruction follows the formula for unimolecular reactions. The destruction by alkali at 30° commences at a point a little below 0·01*N*, and is almost instantaneous at 0·045*N*. The rates of destruction are plotted as curves.

The activity of invertase in acid solutions which are not strong enough to destroy the enzyme have been determined for hydrochloric, hydrobromic, nitric, phosphoric, sulphuric, boric, oxalic, tartaric, citric, and acetic acids. The activity has been found to depend almost entirely on the concentration of hydrogen ions in the solution. The activity of invertase is zero in alkaline solutions, rises to a maximum in very weakly acid solutions, and decreases with increasing acidity.

E. G.

Invertase. Niro Masuda (*Zeitsch. physiol. Chem.*, 1910, 66, 145—151. Compare Salkowski, Abstr., 1909, i, 752).—The addition of yeast gum to an invertase solution which is free, or nearly free, from gum increases the activity of the enzyme to a slight, although perceptible, extent. Invertase solutions (that is, filtered yeast extract) lose almost 70% of their activity on keeping for twenty-four hours, but the activity then diminishes only very slowly. Old preparations full of moulds and bacteria retain their inverting power. Invertase produces slightly more invert sugar in 10% than in 5% sucrose solution. Increase of the amount of ferment does not produce a proportional increase in the amount of invert sugar formed.

E. F. A.

Destruction of Invertase by Acids and Alkalis. H. S. Paine (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, 7, xli—xlii).—Invertase was placed at 30° in various concentrations of hydrochloric acid and sodium hydroxide for different times. All samples were then brought to the optimum acidity in sucrose solutions of the same strength and volume. Action was allowed to take place

for an hour, and the velocity-coefficient calculated from the formula for unimolecular reactions; from this the coefficient of the rate of destruction was derived.

Destruction commenced at about 0·015*N*-acid and 0·01*N*-alkali solution, requiring five to six hours for completion. In 0·05*N*-acid and 0·04*N*-alkali destruction occurred in five minutes. W. D. H.

Studies on Enzyme Action. XIII. Enzymes of the Emulsin Type. Henry E. Armstrong and Edward Horton (*Proc. Roy. Soc.*, 1910, *B*, 82, 349—367. Compare Abstr., 1908, i, 745).—Contrary to the statement of Dunstan, Henry, and Auld (Abstr., 1907, ii, 572), it is shown that phaseolunatin, the glucoside present in *Phaseolus lunatus* seeds, in flax seed, and in cassava is invariably hydrolysed by almond-emulsin, although only to a very small extent. Moreover, amygdalin is found to be as little attacked by the *Phaseolus* enzyme (phaseolunatase) as is phaseolunatin by emulsin, when the comparison is made under molecularly similar conditions.

The observation made by Dunstan, Henry, and Auld (*loc. cit.*), that methyl-α-glucoside is hydrolysed by phaseolunatase, is not confirmed. Similarly, the enzyme was found to be inactive towards maltose. Methyl-β-glucoside, however, is attacked by phaseolunatase, although much less readily than by emulsin, an observation which has not hitherto been recorded.

The authors confirm the statement of Dunstan and his co-workers, that phaseolunatin is hydrolysed by an extract of dried yeast, but attribute this to the action, not of maltase, but of the "emulsin" discovered in yeast by Henry and Auld (Abstr., 1906, ii, 114).

The conclusion arrived at by Dunstan, Henry, and Auld, that phaseolunatin is an α-glucoside, is controverted by the authors. Experiments are described which tend to indicate that the glucose is liberated from phaseolunatin in the β-form, but the question is complicated by the fact that the enzyme itself suffers a change in optical rotatory power when treated with the small quantity of alkali necessary to effect the mutarotation of the liberated glucose. Since all efforts to discover in *Phaseolus* seeds an enzyme capable of effecting the hydrolysis of α-glucosides failed, the conclusion is drawn that phaseolunatin is a β-glucoside, and that the correlated enzyme phaseolunatase is of the β-type.

Although only very slightly active towards amygdalin, phaseolunatase is almost as active as almond-emulsin towards *l*-mandelonitrile-glucoside. This may be partly accounted for by the absence from phaseolunatase of amygdalase, but no explanation is offered of the fact that, whilst phaseolunatase attacks both phaseolunatin and *l*-mandelonitrileglucoside equally, almond-emulsin acts only very slightly on the former glucoside.

Pressed yeast juice and the enzyme extracted from *Anthyllis vulneraria* seed are similarly more active towards *l*-mandelonitrile glucoside than towards amygdalin, and only act very slightly on phaseolunatin. The differences in the activity of vegetable cytase towards the three cyanophoric glucosides are less marked, although in the same direction.

It is pointed out that the experiments assumed by Auld (Trans., 1908, 93, 1277) to prove that the glucose liberated from amygdalin by yeast extract is in the α-form, whilst that set free when l-mandelonitrile glucoside is hydrolysed is in the β-form, are invalidated by the fact that both glucosides are racemised fairly rapidly by alkali, with consequent change in their optical rotatory powers.

A comparison is given of the results obtained when estimating hydrogen cyanide by the method devised by the authors, and by the modification of Fordos and Gelis' method employed by Dunstan and his colleagues. From this it seems that the latter method is only to be preferred in the estimation of quite minute amounts of hydrogen cyanide.

The authors advocate the employment, in experiments with hydrolytic enzymes, of solutions (of the various hydrolytes) of the same molecular concentration, in order that the concordance between the results obtained by different workers (when this exists) may be rendered apparent. E. H.

The Separation of the Racemic Cyanohydrins by Emulsin. Leopold Rosenthaler (*Biochem. Zeitsch.*, 1910, 26, 7—8. Compare Abstr., 1909, i, 74).—l-Benzaldehydecyanohydrin can be obtained from the racemic variety by the action of δ-emulsin when air is led through the mixture. This has the effect of removing one of the products of hydrolysis, namely, the hydrogen cyanide. S. B. S.

Asymmetric Syntheses by means of Enzymes. III. Leopold Rosenthaler (*Biochem. Zeitsch.*, 1910, 26, 1—6).—In addition to the method already described, namely, by heating for a long time at 40—50°, for separating the δ- (hydrolysing) emulsin from the σ- (synthesising) enzyme, the author finds that a separation can also be accomplished by treating the mixtures of enzymes for a short time with acids and then neutralising with alkali. The quantity of acid and time of action must be determined for every sample of emulsin investigated, and great variations are found in the different preparations. The author also describes various other methods attempted for separating the enzymes, which did not lead to the desired effect. S. B. S.

Biology of Enzymes. Action of Heat on the Lipases and Amylases of Pancreatic Juice. Sabato Visco (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 597—603).—The lipolytic power of pancreatic juice was determined by adding to it sweet almond oil and titrating with alcoholic sodium hydroxide the oleic acid formed after the mixture had been a certain time in a thermostat. The amylolytic power was measured by estimating the sugar formed from starch in similar circumstances. It was found that the lipase slowly changes at the ordinary temperature, and loses its activity completely in a few hours at 39—41°. The ferment is not affected by the higher temperature, however, if it has already commenced to act on the oil. The amalyse, when kept at 39—41°, at first shows slightly increased activity, but the latter diminishes, although slowly, on prolonged exposure to that temperature. R. V. S.

Plant Peroxydases. I. New Method of Preparing Peroxydases. A. W. VAN DER HAAR (*Ber.*, 1910, 43, 1321—1327).—Bach (Abstr., 1908, i, 746; this vol., i, 291) has claimed that both peroxydases and oxydases can be obtained absolutely free from manganese and iron. Peroxydase has now been purified by the author a stage further than by Bach, until all coagulable protein had been removed, but it has not been possible to remove absolutely all manganese. After precipitation of impurities by basic lead acetate, the proteins can be coagulated by heating the solution to 90° without destroying the peroxydase. Throughout the process of purification the oxidising power was contrasted with the amount of manganese present, but no relation between these two factors was evident. E. F. A.

Plant Peroxydases. II. Hedera-Peroxydase, a Glucoprotein. A. W. VAN DER HAAR (*Ber.*, 1910, 43, 1327—1329).—A carefully purified peroxydase preparation from the leaves of *Hedera helix* contained 2% of ash, and the solution, which lacked other known enzymes, showed the biuret, xanthoprotein, and Millon's reactions; it contained organically combined nitrogen and sulphur, but was free from phosphorus. When boiled with 3% hydrochloric acid, it acquired the power of reducing Fehling's solution, and formed a phenylosazone, m. p. 165°. In addition, the peroxydase was non-coagulable, and could not be salted out. It is regarded in consequence as a glucoprotein. It contained 0·0007% of manganese, equivalent to 0·03% of the ash. The peroxydase from potatoes also yielded a carbohydrate on treatment with acids. E. F. A.

Action of Haloid Derivatives of Sulphur on Organomagnesium Compounds. ENOS FERRARIO [and, in part, H. VINAY] (*Bull. Soc. chim.*, 1910, [iv], 7, 518—527).—The investigation of the action of sulphur chloride, dichloride, and tetrachloride on aromatic and aliphatic magnesium haloid compounds showed that sulphurisation, chlorination, and condensation proceeded simultaneously; thus with sulphur dichloride the following reactions probably occurred: $2PhMgBr + SCl_2 = SPh_2 + 2MgBrCl$; $2PhMgBr + 2SCl_2 = 2PhCl + 2MgBrCl + S_2$; $4PhMgBr + 2SCl_2 = 2Ph-Ph + 4MgBrCl + S_2$; $2PhS\cdot MgBr + SCl_2 = S_3Ph_2 + 2MgBrCl$. The products of the reaction were separated by fractional distillation under diminished pressure.

The mixture, obtained by the action of sulphur chloride on magnesium phenyl bromide and the addition of water, contained chlorobenzene, bromobenzene, phenyl sulphide, diphenyl and phenyl disulphide, trisulphide, and tetrasulphide. Sulphur dichloride with the same compound furnished the same products as did also sulphur tetrachloride, except that in the latter case more chlorobenzene was formed. In this reaction the tetrachloride behaved as a mixture of sulphur dichloride and chlorine.

Sulphur chloride reacted with magnesium methyl iodide to give methyl chloride and methyl sulphide, disulphide, and trisulphide. The action with magnesium ethyl bromide was analogous, ethyl chloride, sulphide, and disulphide being formed. T. A. H.

Organic Chemistry.

Critical Constants of Acetylene and Cyanogen. Ettore Cardoso and Georges Baume (*Compt. rend.*, 1910, 151, 141—143).—The following values have been obtained for the critical constants of pure acetylene and cyanogen. Acetylene has a critical temperature 35·5°, and critical pressure 61·5 atmospheres (compare Mathias, Abstr., 1909, ii, 552). Cyanogen has a critical temperature 128·3°; pressure, 59·6 atmospheres. The author considers that the cyanogen employed in Dewar's determinations was not free from air, and that consequently the results obtained were too low (Abstr., 1885, 331).

W. O. W.

The Decomposition of Certain Salts of Silver. Angelo Angeli and L. Alessandri (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 784—793. Compare Abstr., 1909, i, 739).—The dinitro-derivatives of stilbene have been stated to be converted into resins by the action of alkali, whilst the compounds obtained by the authors from the silver salt of *ω-iso*nitrotoluene yield definite compounds. It is now shown that the action of sodium ethoxide on *α*-dinitrostilbene yields the compound $OEt\cdot CHPh\cdot CHPh\cdot NO_2$, identical with that obtained by the authors, and yielding the compound $CHPh{:}CPh\cdot NO_2$ when acted on with piperidine.

Other nitro-derivatives react in a similar manner. The silver salt of nitroethane decomposes, yielding a *dinitrobutane*,

$$NO_2\cdot CHMe\cdot CHMe\cdot NO_2,$$

which melts at 41° and decomposes at 150°, but may be distilled under reduced pressure. At the same time a small quantity of the compound $CHMe{:}CMe\cdot NO_2$ appears to be formed.

The pure dinitro-compound is decomposed by potassium methoxide, but the original oil yields large, bright yellow crystals of a salt, $C_8H_8O_5N_4K_2$, apparently a condensation product.

It was not found possible to reduce the dinitrobutane directly to diacetyldioxime, a hydroxylamine derivative being formed, which is not readily oxidised to the dioxime. The reduction may, however, be effected by means of zinc dust and acetic acid in alcohol, concentrating the filtrate, and adding hydrochloric acid, followed by the addition of an excess of ammonium chloride, ammonia, and nickel sulphate, afterwards passing a current of air. A heavy, pink precipitate of the nickel compound of diacetyldioxime is obtained (Tschugaeff, Abstr., 1905, ii, 613), and yields the dioxime when decomposed with acid.

The silver salt of nitropentane yields colourless prisms of *dinitrodecane*, $C_{10}H_{20}O_4N_2$, m. p. 109—110°.

Piperonaldoxime, nitrocinnamene, and phenyldiazonitroethane also yield unstable salts, but definite compounds have not been isolated from their products of decomposition.

C. H. D.

Action of Metallic Oxides on the Primary Alcohols. Paul Sabatier and Alphonse Mailhe (*Ann. Chim. Phys.*, 1910, [viii], 20, 289—352).—Mainly a résumé of work published by the present authors and others (compare Jahn, Abstr., 1880, 794; Grigorieff, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 173; *Bull. Soc. chim.*, 1902, [iii], 26, 612; Ipatieff, Abstr., 1901, i, 248; 1902, i, 335; 1903, i, 593; Sabatier and Mailhe, Abstr., 1908, i, 594, 713; 1909, i, 546; this vol., i, 294; Senderens, Abstr., 1908, ii, 166; 1909, i, 127, 286; Sabatier and Senderens, 1905, i, 333, 401). Contrary to the statement made previously (Abstr., 1909, i, 546), methyl alcohol when decomposed by titanium oxide gives formaldehyde.

A table is given showing the composition of the gas evolved, and its rate of evolution, when a fixed quantity of ethyl alcohol is decomposed by the various oxides examined.

An explanation similar to that proposed for the decompositions effected by finely-divided metals is suggested for the catalyses produced by the oxides. E. H.

Preparation of Pyruvic Acid. Alfred Wohl and Rudolf Maag (*Ber.*, 1910, 43, 2188—2189).—A 60% yield of pure pyruvic acid, b. p. 59—60°/12 mm., can be obtained by distilling a mixture of 500 grams of tartaric acid and 780 grams of commercial potassium hydrogen sulphate from a copper retort of about 2 litres capacity. The process requires about thirty minutes, and no frothing occurs. As the metal is corroded by the sulphate, it is advisable to cover the interior of the retort with asbestos paper and water glass. The receiver is well cooled, and is provided with an upright condenser, the upper end of which is closed with a plug of cotton wool. The crude distillate is purified by fractional distillation under reduced pressure. J. J. S.

Degradation of Cholic Acid. II. The Distillation Products of Cholic and Bilianic Acids. Otto von Fürth and Emil Lenk (*Biochem. Zeitsch.*, 1910, 26, 406—434).—Two main products were obtained by the distillation both of cholic and bilianic acid, the one of oily and the other of wax-like nature. The oily product is a hydrocarbon with something between 12 and 17 carbon atoms (as it gave varying numbers for the molecular weight determined by the ebullioscopic method in various solvents). It readily resinifies. The wax-like substance contains oxygen. The authors give an account of the action of halogens of permanganate and of nitric acid on the oily substance. No products have yet been isolated in a pure state. S. B. S.

Preparation of Cystine. Otto Folin (*J. Biol. Chem.*, 1910, 8, 9—10).—Cystine is easily prepared from wool by the following method, which differs mainly from Mörner's in the use of strong acid; 200 c.c. of strong hydrochloric acid to each 100 grams of wool are boiled in a flask (with a condenser consisting of a tube 2 or 3 feet long) until the biuret test is negative, usually three to five hours. Solid sodium acetate is added until the Congo-red reaction for mineral acid

is negative; a dark heavy precipitate, which contains practically all the cystine is obtained; this is filtered and washed with cold water. The filtrate on keeping deposits a second precipitate, consisting mainly of tyrosine. The crude cystine is dissolved in 3 to 5% hydrochloric acid and decolorised with bone-black, which has been previously digested with dilute hydrochloric acid to remove the calcium phosphate. The filtrate is heated to boiling, and the cystine precipitated by the slow addition of hot concentrated sodium acetate solution. W. D. H.

Action of Ozone on Organic Compounds. II. Carl D. Harries (*Annalen*, 1910, **374**, 288—368. Compare Abstr., 1906, i, 225).—The paper contains a discussion of work published during the last five years on the mode of attack of ozone on various classes of organic compounds, the behaviour of ozone derivatives during fission by water or other reagents, the constitution of the ozonides, the special behaviour towards ozone of substances containing different kinds of double linkings, the behaviour of the solvent during ozonisation, a description of the ozonising apparatus, and the effect of varying concentrations of ozone.

The following new work is described. Ethyl alcohol has been ozonised in the hope of showing that the first step in the oxidation is the formation of Baeyer and Villiger's ethyl hydroperoxide, EtO·OH. The *substance* obtained, however, is not identical with, but must be nearly allied to, ethyl hydroperoxide; possibly it is the tautomeric peroxide, $\frac{Et}{H}>O:O$. It has b. p. 55—56°/10 mm., $D^{21\cdot5}_{21\cdot5}$ 1·028, n_D 1·40924, explodes violently when heated, contains 11·3% of active oxygen, reduces Fehling's solution and ammoniacal silver nitrate, and yields hydrogen peroxide and acetaldehyde when decomposed by water. The oxidation of β-hydroxypropioacetal by ozone yields β-hydroxypropaldehyde, not the semi-acetal of malondialdehyde as previously stated (Harries, Abstr., 1904, i, 15).

[By Rudolf Koetschau.]—Langheld has shown that by direct ozonisation heptaldehyde yields a peroxide, $C_7H_{14}O_2$. When treated with 15% ozone in ethyl chloride, or with 7% ozone in methyl chloride, the aldehyde yields a *substance*, D^{17}_{17} 0·9504, n^{17}_D 1·42867, the composition of which approximates to the formula $C_7H_{14}O_3$. Similarly, octaldehyde, when ozonised in ethyl chloride by 15% ozone, yields a *peroxide*, $C_8H_{16}O_2$, D^{19}_{19} 0·9088, n^{19}_D 1·42767, or by more prolonged action a *substance*, D^{19}_{19} 0·9497, n^{19}_D 1·43267, approximating to the composition $C_8H_{16}O_3$. By direct ozonisation with 7% ozone at 0°, nonaldehyde yields a *peroxide*, $C_9H_{18}O_2$, m. p. 6°, which is not identical with the peroxide, m. p. 73°, obtained by the decomposition of oleic acid ozonide; in methyl chloride the aldehyde is converted by 7% ozone into a *substance*, D^{21}_{21} 0·9334, n^{21}_D 1·43167, the composition of which approximates to $C_9H_{18}O_3$. *iso*Valeraldehyde yields a *peroxide*, $C_5H_{10}O_2$, D^{23}_{23} 0·9462, n^{23}_D 1·40826, by direct treatment with 15% ozone in a freezing mixture, and a *substance*, $C_5H_{10}O_3$(?), n^{21}_D 1·40335, when ozonised in ethyl chloride. *iso*Butaldehyde and acetaldehyde behave in a similar manner. Formaldehyde in methyl chloride is quantitatively

converted into trioxymethylene by treatment with ozone. By treatment with sodium hydroxide, the preceding peroxides are converted into the sodium salts of the corresponding acids. The fatty acids do not yield per-acids by treatment with ozone, but are merely oxidised.

[With H. O. Türk.]—To the results obtained by Harries and Türk by the exhaustive ozonisation of mesityl oxide and phorone (Abstr., 1905, i, 413) the following are to be added. By treatment with 12—14% ozone in an atmosphere of dry carbon dioxide, mesityl oxide, cooled by a freezing mixture, yields a normal *ozonide*, $C_6H_{10}O_4$, $D_{18\cdot5}^{18\cdot5}$ 1·0754, $n_D^{18\cdot5}$ 1·39409, which is decomposed by water, yielding acetone, methylglyoxal, and formic and acetic acids; when carefully heated at 105°, the ozonide yields carbon dioxide, acetone, acetone peroxide, formic and acetic acids, methylglyoxal, and mesityl oxide, which is identified in the form of its *p*-nitrophenylhydrazone.

By ozonisation in carbon tetrachloride, care being taken to avoid an excess of ozone, methylheptenone yields a normal *ozonide*, $C_8H_{14}O_4$, which resembles Langheld's perozonide in many respects. It is decomposed by water, yielding acetone peroxide, acetone, lævulic acid, lævulaldehyde (isolated as phenylmethyldihydropyridazine), and a small amount of a peroxide of the last.

Mesoxaldialdehyde, in the form of its *tris*-p-*nitrophenylhydrazone*, m. p. 297° (decomp.), has now been definitely detected amongst the products of decomposition of phorone diozonide by water (compare Harries and Türk, *loc. cit.*). When a chloroform solution of phorone is incompletely ozonised, a *monozonide* seems to be formed, since dimethylacrylic acid occurs amongst its products of decomposition by water. Mesoxaldialdehyde, together with benzaldehyde and benzoic acid, is formed by decomposing with water the viscous, yellow oil formed by ozonising a chloroform solution of dibenzylideneacetone until the greenish-yellow colour has disappeared.

[By Karl Kircher.]—It has been stated previously (Harries and Kircher, Abstr., 1907, i, 466) that the ozonide of β-benzylidenelævulic acid is decomposed by water, yielding benzaldehyde, benzoic acid, and diacetylcarboxylic acid, and also that diacetylcarboxylic acid is a comparatively stable compound. It is now found that malonic acid is also present amongst the products of decomposition of the ozonide, and also that diacetylcarboxylic acid is an unstable substance, being partially decomposed even by the evaporation of its aqueous solution in a vacuum. Since the products of its decomposition are malonic and acetic acids, it seems very probable that the decomposition of β-benzylidenelævulic acid ozonide involves the production of a peroxide, thus:

$$\begin{array}{l} CHPh\cdot CAc\cdot CH_2\cdot CO_2H \\ O{-}O{-}O \end{array} \longrightarrow PhCHO + \begin{array}{l} O \\ O \end{array}\!\!>\!C\!<\!\begin{array}{l} CO\cdot CH_3 \\ CH_2\cdot CO_2H \end{array} \xrightarrow{H_2O}$$

$$CH_3\cdot CO_2H + CH_2(CO_2H)_2.$$

Diacetylcarboxylic acid forms a *bis*-p-*nitrophenylhydrazone*, m. p. 295° (decomp.), crystallising in red prisms, and a *bis-semicarbazone*, m. p. 240° (decomp.).

[By Walter Franck.]—Further information is given respecting the ozonides of oleic acid (compare Harries and Franck, Abstr., 1909, i, 131). The normal ozonide is always produced, independent of the concentration of the ozone, when care is taken, by testing with bromine

in acetic acid, to avoid any excess of the amount of ozone theoretically required; directly this limit is exceeded, the perozonide is formed. The normal ozonide is decomposed by hot glacial acetic acid, yielding nonaldehyde and its peroxide, nonolic acid, azelaic acid, and its peroxide and semialdehyde. Decomposition by glacial acetic and formic acids prevents the formation of peroxides, but otherwise gives the same products. The decomposition of an ethereal solution of the ozonide by moist ethereal sulphur dioxide or by aluminium amalgam also yields the same products. The normal ozonide of oleic acid forms salts, of which the *ammonium*, *sodium*, and *copper* salts are described, when care is taken to exclude moisture and to prevent rise of temperature. Nonaldehyde peroxide, m. p. 72°, b. p. 80—90°/13 mm., is changed to sodium nonoate by sodium hydroxide, and liberates only about 50% of the theoretical quantity of iodine from acidified potassium iodide in consequence of the change of about one-half of the peroxide into the isomeric acid.

When oleic acid is submitted to prolonged treatment with 10% ozone, or when its solution in glacial acetic acid is treated with 16—18% ozone for four hours, a *super-perozonide*, $C_{18}H_{34}O_7$, is formed, which has D_{22}^{22} 1·079, n_D^{22} 1·46817, is not particularly explosive, and yields by decomposition with warm water the same products as the other ozonides of oleic acid.

The normal *ozonide*, $C_{18}H_{34}O_6$, D_{20}^{20} 1·027, n_D^{20} 1·46171, of elaidic acid is prepared in a similar manner to, and does not differ in any respect from, the normal ozonide of oleic acid; it has not yet been settled whether the two are identical. C. S.

The Scission of Sugars. Synthesis of Sugar from Formaldehyde. Walther Löb and Georg Pulvermacher (*Biochem. Zeitsch.*, 1910, **26**, 231—237. Compare this vol., i, 95).—Experiments were carried out to determine whether the equilibrium between formaldehyde and the aldehydes with more carbon atoms (hexoses and pentoses) was the same in the building-up process from aldehydes as in the degrading processes from sugars, when the same substances are present at the same time in a mixture. The question could not be definitely answered, owing to the secondary process affecting only the formaldehyde, by means of which it was converted into methyl alcohol and acraldehyde. On treatment of formaldehyde solutions with lead hydroxide, a pentose seemed to be formed, which could not be isolated in the form of a pure osazone. Saccharic acid could be identified. S. B. S.

Phosphoric Esters of Some Polyhydric Alcohols and Carbohydrates. Angelo Contardi (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 823—827. Compare this vol., i, 157).—It is shown that certain polyhydroxylic compounds combine with phosphoric acid without undergoing any change of structure, a fact of importance in studying naturally occurring compounds.

When 25 grams of mannitol are heated for ten hours with 120 grams of phosphoric acid, D 1·7, to 120—130°, the product being decolorised with animal charcoal and purified by means of the barium

salt, a syrupy liquid, having the composition $C_6H_{20}O_{24}P_6$, is obtained, and is thus *mannitol hexaphosphate*. Quercitol yields a *pentaphosphate*, $C_6H_{17}O_{20}P_5$, whilst dextrose forms a *heptaphosphate*, $C_6H_{20}O_{28}P_7$, the aldehyde group behaving as two hydroxyl groups. C. H. D.

Phosphoric Acid Esters of Carbohydrates. II. Sucrosesulphuric Acid and the Phosphoration of Protein. Carl Neuberg and Hugo Pollak (*Ber.*, 1910, **43**, 2060—2068; *Biochem. Zeitsch.*, 1910, **26**, 514—534. Compare this vol., i, 157).—Dextrose dissolved in water and mixed with finely-divided calcium carbonate is well cooled and continuously shaken from eight to ten hours with phosphoryl chloride dissolved in chloroform. The liquid is then concentrated in a vacuum, and the *calcium salt* of *dextrose phosphoric acid ester* precipitated by pouring into alcohol. It is a colourless, soluble powder, stable in the atmosphere, and reduces Fehling's solution. It only shows the reactions of phosphoric acid after hydrolysis with boiling mineral acids, and is not fermentable until hydrolysed.

To prepare sucrosesulphuric acid, potassium pyrosulphate is slowly added to a mixture of sucrose and potassium hydroxide at 60—70°. After twenty-four hours, inorganic sulphuric acid is removed with barium hydroxide and *barium sucrosesulphate*, obtained as a colourless powder which only reduces Fehling's solution after hydrolysis. It has $[\alpha]_D^{29}$ +26·09°. The sulphuric acid is very firmly bound in the molecule, but if the equivalent quantity of cold hydrochloric acid is added to the barium salt, the liquid obtained reduces Fehling's solution after a time. The *calcium* salt is similar; it is not fermentable.

The simple amino-acids react with phosphoryl chloride in presence of alkali to form organic phosphoric acid compounds, but these could not be isolated. The proteins behave similarly, but in this case the phosphorus compounds are precipitated by acetic acid. These phospho-proteins are similar to the natural products, and are digested by trypsin and pepsin. E. F. A.

Stachyose and Lupeose. Ernst Schulze (*Ber.*, 1910, **43**, 2230—2234).—Lupeose (β-galactan: Abstr., 1892, 1171) from *Lupinus luteus* and *L. angustifolius* has the same optical rotation and gives the same yield of mucic acid on oxidation as stachyose, whereby saccharic acid is also formed. It is a tetrasaccharide composed of residues of galactose (2), dextrose, and lævulose, but since it cannot be caused to crystallise in the same way as stachyose, the two are not yet regarded as identical. When purified by pouring the aqueous solution into methyl alcohol, and precipitating this solution with absolute ethyl alcohol, it has $[\alpha]_D$ +148°. E. F. A.

Oxidation and Hydrolysis of Glycogen Under the Action of Hydrogen Peroxide. Mme. Z. Gatin-Gružewska (*Bull. Soc. chim.*, 1910, [iv], **7**, 744—747. Compare Würster, Abstr., 1887, 683; Asboth, Abstr., 1893, i, 384; Gatin-Gružewska, Abstr., 1909, i, 209).—If a 1% solution (100 c.c.) of glycogen is mixed with pure hydrogen peroxide (5 c.c.) and kept at 37°, the opalescent liquid

gradually becomes more and more limpid, and at the end of five days is quite transparent, when it is no longer coloured by iodine. Under the same conditions, solutions of amylopectin take a shorter, and of amylose a longer, time to become transparent. The transparent solution, when treated with ten volumes of alcohol, gives a precipitate having all the properties of an achroodextrin, the amount of which diminishes and has entirely disappeared at the end of the twelfth day. The same changes occur if the liquid is previously rendered slightly alkaline with sodium hydrogen carbonate. The course of the oxidation can be traced by withdrawing samples from the solution at intervals of twenty-four hours and estimating the acidity by titration with standard alkali, whilst the undecomposed hydrogen peroxide may be estimated with permanganate. To determine the reducing power towards Fehling's solution, the hydrogen peroxide is first decomposed by adding platinum black to the neutralised sample.

Examination of the curves tracing the rate of decomposition of the hydrogen peroxide shows that 5 c.c. of hydrogen peroxide decompose most rapidly in 100 c.c. of water, only traces remaining after ten days, less rapidly in a 1% glycogen solution, about 16% being left at the end of twenty-three days, and still less rapidly in a starch solution, 50% being still undecomposed after twenty-three days. In more concentrated solutions the decomposition is more rapid, probably owing to the greater acidity and different character of the colloid. The change in the reducing power of glycogen is slower, and in acidity is faster, than the corresponding changes for starch. Whilst the action of hydrogen peroxide on glycogen is more energetic than that on starch, the converse is true of the action of the amylase from the pancreatic juice of the dog on these two substances. E. H.

New Method of Preparation of Primary and Secondary Amines from Ketones. Karl Löffler (*Ber.*, 1910, **43**, 2031—2035).—By the action of ammonia or methylamine on ketones and subsequent reduction with sodium ethoxide, primary and secondary amines are readily obtained in good yields. It is assumed that the imine, $X_1X_2C{:}NR$, is the intermediate product of the change being formed by elimination of water between ketone and ammonia, or from a ketoammonia compound. Thus from acetone and ammonia a mixture of *iso*propylamine and di*iso*propylamine is formed; the formation of the latter is explained as due to the *iso*propylamine formed reacting with unchanged acetone in the same manner. *iso*Propylamine aurichloride (H_2O) forms matted plates, m. p. 72—73° [Fenner and Tafel (Abstr., 1900, i, 111) give m. p. 131—135°, which probably refers to the nearly dry salt]. The *aurichloride* of di-*iso*propylamine separates in masses of intergrown needles, m. p. 169—170°.

sec.-Amylamine is obtained in the same way from methyl propyl ketone and ammonia; the platinichloride forms glistening plates, decomp. 215°; the normal oxalate has m. p. 226°; the sulphate crystallises in colourless plates. E. F. A.

Synthetic Homocholine. Friedrich Kutscher (*Zeitsch. physiol. Chem.*, 1910, **67**, 296).—In reference to the work of Malengreau and

Lebailly on this subject (this vol., i, 545), it is pointed out that synthetic homocholine was prepared by Berlin in the author's laboratory, but his results are not yet published. W. D. H.

Additions to the Papers on ε-Amino-α-guanidinohexoic Acid and New Syntheses of Aminohydroxy-acids and of Piperidone Derivatives. Emil Fischer and Géza Zemplén (*Ber*, 1910, **43**, 2189—2192. Compare this vol., i, 100, 305).—The dihydrochloride of an anhydride of ε amino-α-guanidinohexoic acid was obtained by the decomposition of ε-benzoylamino-α-guanidinohexoic acid with hydrochloric acid. The free base, *ε-amino-α-guanidinohexoic anhydride*, $C_7H_{14}ON_4$, is a colourless, crystalline powder, which turns bright red at 175—185°, and decomposes at 190° to a brownish-yellow liquid. The *platinichloride* is a yellow, crystalline powder, which becomes grey at 220—230°, and decomposes at 230—240°.

The amorphous compound obtained by the hydrolysis of gelatin, previously described as possessing some points of resemblance to the synthetic β-hydroxy-α-piperidone, is now found to be a mixture of anhydrides of α-amino-acids. E. F. A.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XIV. Phosphorescence of Organic Sulphur Compounds by Spontaneous Oxidation. Marcel Delépine (*Bull. Soc. chim.*, 1910, [iv], 7, 722—724).—In addition to the compounds containing the group S:ĊO· already described (this vol., i, 295), which are phosphorescent by spontaneous combustion, *methyl sulphocarbonic chloride*, Cl·CS·OMe, b. p. 107—108°, and ethyl sulphocarbonic chloride, Cl·CS·OEt, are observed to fume in the air and phosphoresce strongly with an ozone-like odour. When the methyl ester is treated with magnesium methyl iodide, it gives the *compound*, Me·CS·OMe, b. p. 87—89°, which also fumes and phosphoresces strongly. The only compound, not containing the above group, which oxidises with brilliant phosphorescence is carbon chlorosulphide, $SCCl_2$. Methyl and ethyl methyl thiocarbonate, SMe·CO·OR, methyl ethyl thiocarbonate,

SEt·CO·OMe,

methyl dithiocarbonate, $CO(SMe)_2$, and methyl dimethothiocarbamate, SMe·CO·NMe_2, which contain the grouping O:ĊS·, and the iminothiocarbonic esters, NMe:C(SMe)·OMe, NMe:C(SEt)·OMe, and NEt:C(SMe)·OMe, which contain the grouping $:C<^{O\cdot}_{S\cdot}$ (see following abstract), do not phosphoresce. Tetramethyl-, tetraethyl-, and tetrapropyl-*iso*thiocarbimides, NR:C(SR)·NR_2, and the isomeric tetra-alkylthiocarbamides, $CS[NR_2]_2$, which are formed by replacing the ·OR-group of the phosphorescent sulphocarbamic esters, NRR′·CS·OR, with the group ·NRR′, as well as the thiosulphocarbamic esters,

NRR′·CS·SR″,

are similarly inactive. The sulphocarbamic esters, NH_2·CS·OR or NHR′·CS·OR, which contain a hydrogen atom combined with the nitrogen, do not, unlike their alkyl derivatives, phosphoresce by spontaneous oxidation.

It is suggested that the readiness with which the compounds con-

taining the group S:CO· are oxidised is due to the residual affinity of the sulphur and carbon atoms. E. H.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XV. Iminothiocarbonic Esters of the Aliphatic Series: $RN{:}C(OR)(SR_1)$. Marcel Delépine (*Bull. Soc. chim.*, 1910, [iv], 7, 724—727).—Some of the iminothiocarbonic esters, which contain the grouping $:C<^{S\cdot}_{O\cdot}$, have been prepared for comparison with the compounds (preceding abstract) containing the grouping S:C·O·, which are phosphorescent by spontaneous oxidation. Hitherto only the aromatic derivatives of this series have been prepared (compare Liebermann, Abstr., 1882, 296; Wheeler and Dustin, Abstr., 1901, i, 24).

When the sodium salts of the thiocarbamic esters prepared according to Roschdestvensky's method (this vol., i, 107) are treated with alkyl iodides they probably react in the tautomeric form, thus:

$$NR{:}C(OR)\cdot SNa + IR' = NR{:}C(OR)\cdot SR' + NaI,$$

giving the aliphatic iminothiocarbonic esters. The latter are colourless, mobile liquids, boiling almost 50° lower than, and appreciably less dense than, the corresponding iminodithiocarbonic esters, which they resemble in odour. The iminothiocarbonic esters are weak bases, soluble in dilute acids, but readily displaced by alkalis or ammonia, neutral to litmus and phenolphthalein, but exactly mono-acid towards helianthin. They are hydrolysed by boiling dilute acids into the amine and thiocarbonic ester. The iminothiocarbonic esters, like the dithiocompounds, lose the ·SR′ group when treated with silver nitrate or mercuric chloride.

Neither the iminothiocarbonic esters nor the sulphourethanes, NHR·CS·OR′, obtained intermediately, nor the thiocarbonic esters, CO(OR)(SR′), formed on hydrolysis, fume or phosphoresce when brought into contact with the air. The picrates of the first-named compounds form well-defined, yellow crystals.

Dimethyl methyliminothiolcarbonate, NMe:C(SMe)·OMe, a liquid, b. p. 142—144°, D_4^0 1·0654, D_4^{19} 1·0457, n_D^{20} 1·48458, when hydrolysed gives the hitherto unknown *methyl methyl thiolcarbonate*, CO(SMe)·OMe, which is a colourless liquid having an ethereal odour, b. p. 120—121°, D_4^0 1·1452, $D_4^{21\cdot5}$ 1·1203, n_D^{23} 1·45242; the *picrate* of the former has m. p. 110°.

Methyl ethyl methyliminothiolcarbonate, NMe:C(SEt)·OMe, has b. p. 158—160°, D_4^0 1·0320, D_4^{19} 1·0125, $n_D^{20\cdot5}$ 1·48189; the *picrate* has m. p. 100°. *Dimethyl ethyliminothiolcarbonate*, NEt:C(SMe)·OMe, has b. p. 154—155°, D_4^0 1·02545, D_4^{19} 1·0056, $n_D^{20\cdot5}$ 1·47838; the *picrate* has m. p. 94°. Instead of the values previously given, the author finds for dimethyl thioncarbonate, $CS(OMe)_2$, D_4^0 1·13065, D_4^{24} 1·1028, n_D^{24} 1·45962. The latter compound is distinguished from the isomeride, SMe·CO·OMe, by reacting immediately with silver nitrate, silver sulphide being precipitated. E. H.

A Simple Method of Preparation of Pure Cyanamide. Fritz Baum (*Biochem. Zeitsch.*, 1910, 26, 325—332).—Seventy-five grams of

calcium nitride are stirred for half an hour with 400 c.c. of water. The process is repeated with a second quantity of water, which is finally used for treatment of a second batch of nitride. A third extract with water of the first batch is used for a second treatment of the second batch, and then for a first treatment of a third batch of nitride, etc. Finally, an extract is obtained which has been employed for treatment of four lots of nitride, and which is a strong solution of cyanamide. This is neutralised with sulphuric acid, separated from the precipitated calcium sulphate, and the liquid is then concentrated in a vacuum. On cooling, the residue crystallises, and the cyanamide is then separated from the calcium sulphate, and dicyandiamide formed as a by-product by extraction with ether. The ether is diluted, as another by-product is often precipitated which is not soluble in the dilute solution of cyanamide in ether. After distilling off the ether, pure cyanamide which distils at 143—144°/18 mm., is obtained. On treatment with methyl alcohol and hydrochloric acid, it yields the methyl ether of *iso*carbamide. S. B. S.

Double Thiocyanates of Bivalent Copper and of Cobalt with Organic Bases. J. Calzolari (*Ber.*, 1910, 43, 2217—2219).—Cupric thiocyanate, although insoluble in, and decomposed by, water, dissolves unchanged in concentrated solutions of an alkali thiocyanate. From the solution, however, thiocyanates of bivalent copper cannot be isolated, since they readily decompose, especially on warming, with the deposition of cuprous thiocyanate. The following double thiocyanates of bivalent copper with organic bases can, however, be readily isolated.

Tripyridinium cupric thiocyanate, $Cu(CNS)_2,3Py,HCNS$, is obtained as a reddish-brown precipitate by adding a concentrated solution of copper nitrate to a saturated solution of ammonium thiocyanate until the black precipitate first formed redissolves, filtering, and then adding a concentrated solution of pyridine thiocyanate.

Dihexamethylenetetramine cupric thiocyanate,

$$Cu(CNS)_2,2C_6H_{12}N_4,HCNS,$$

separates as a light green, crystalline precipitate when hexamethylenetetramine thiocyanate is used instead of pyridine thiocyanate. Since the compound is anhydrous, the green colour, which is different from the reddish-brown colour of the solutions of cupric thiocyanate in concentrated solutions of the alkali thiocyanates, must depend on the organic base. This is confirmed by the fact that *dihexamethylenetetramine cobalt thiocyanate*, $Co(CNS)_2,2C_6H_{12}N_4,HCNS$, which was prepared in a similar manner to the corresponding copper compound, forms lilac-coloured crystals, whereas the thiocyanates of cobalt are blue.

Hexamethylenetetramine thiocyanate is precipitated from a saturated solution of ammonium thiocyanate (1 mol.) and hexamethylenetetramine (1 mol.) on the addition of hydrogen chloride; it forms large, transparent, colourless, monoclinic prisms. T. S. P.

Crystallographical and Optical Investigations of Organic Compounds. C. Blass (*Zeitsch. Kryst. Min.*, 1910, 48, 20—44).—The following crystallographic determinations are given: Potassium

molybdenum hexathiocyanate, pseudohexagonal [$a:c=1:0{\cdot}67197$]; the ammonium salt, rhombic [$a:b:c=0{\cdot}60721:1:0{\cdot}88406$], and the sodium salt, triclinic [$b:c=1:0{\cdot}98114$]. Potassium chromihexathiocyanate, pseudohexagonal [$a:c=1:0{\cdot}67934$], the ammonium salt, rhombic [$a:b:c=0{\cdot}61109:1:0\ 87651$], and the sodium salt, triclinic.

Corydine is tetragonal trapezohedric [$a:c=1:0{\cdot}39896$], and has $[\alpha]_D^{20}$ $+204{\cdot}35°$ in chloroform; bulbocapnine, rhombic hemihedral [$a:b:c=0{\cdot}72520:1:0{\cdot}71792$], $[\alpha]_D^{20}$ $+237{\cdot}1°$ in chloroform; bulbocapnine monomethyl ether, tetragonal hemihedral [$a:c=1:1{\cdot}05540$], $[\alpha]_D^{20}$ $+247{\cdot}2°$ in chloroform; monobenzoylbulbocapnine, rhombic [$a:b:c=0{\cdot}89437:1:0{\cdot}63116$], $[\alpha]_D^{20}$ $+92{\cdot}7°$ in chloroform; ephedrinephenylthiocarbamide, rhombic hemihedral sphenoidal [$a:b:c=0{\cdot}81703:1:0{\cdot}42834$], $[\alpha]_D^{20}$ $-105{\cdot}1°$ in abs. alcohol; ψ-ephedrinethiocarbamide, rhombic [$a:b:c=0{\cdot}37134:1:0{\cdot}62669$], $[\alpha]_D^{20}$ $+22{\cdot}8°$ in absolute alcohol.

Patchouli-alcohol, hexagonal [$a:c=1:0{\cdot}56528$], $[\alpha]_D^{20}$ $-124{\cdot}5°$ in alcohol; cedrol, rhombic [$a:b:c=0{\cdot}98385:1:0{\cdot}70502$], $[\alpha]_D^{20}$ $-84°$ to $-61°$; cypress camphor, rhombic [$a:b:c=0{\cdot}98844:1:0{\cdot}71772$], is optically inactive; guaiol (champacol), trigonal pyramidal [$a:c=1:0{\cdot}54959$], $[\alpha]_D$ $-29{\cdot}8°$; benzoyleugenol, monoclinic [$a:b:c=1{\cdot}5829:1:1{\cdot}0713$]; acetyl*iso*eugenol, rhombic [$a:b:c=0{\cdot}68815:1:0{\cdot}97672$]; *iso*apiole, monoclinic [$a:b:c=0{\cdot}876502:1:1{\cdot}7878$]; menthyl benzoate, rhombic [$a:b:c=0{\cdot}76134:1:0{\cdot}24476$], $[\alpha]_D^{20}$ $-90{\cdot}72°$; guaiolglycerol, rhombic [$a:b:c=0{\cdot}23916:1$].

α'-Methyl-α-ethylolpiperidine, rhombic [$a:b:c=0{\cdot}6777:1:0{\cdot}61179$].

T. S. P.

The Destruction of Cyanide. James Moir and James Gray (*Chem. Met. Min. Soc. S.A.*, 1910, 10, 433—441).—Experiments are described which had for their object the destruction of cyanide. Complete destruction can be achieved by several methods (such as the action of silver and cuprous salts and of ammonium disulphide), but the ferrocyanide reaction is the only one which would be commercially successful on the Rand. A thorough investigation of this reaction showed (1) that when *excess* of alkali is used, the amount of ferrocyanide formed is less than when smaller quantities of alkali are present; (2) that rise of temperature above 20° is harmful to the reaction; (3) that the results are nearly independent of dilution; (4) that the reaction is as complete in five to ten seconds as after a long time, and (5) that unless the alkalinity is most carefully adjusted to suit the amount of iron used, an excess of ferrous solution gives no better results than the theoretical quantity (that required by the equation: $6KCN + 2FeSO_4,7H_2O = K_2Fe[Fe(CN)_6] + 2K_2SO_4 + 7H_2O$).

In no case have the authors succeeded in obtaining entire destruction of the cyanide used, although in several cases they obtained a reaction sufficiently complete for all industrial purposes, the cyanide having been reduced to three or four parts per million.

It is pointed out that a solution containing free hydrocyanic acid cannot be correctly estimated with silver nitrate; for correct results it is necessary to add an excess of alkali before titration with the silver nitrate. T. S. P.

Perylene, a Highly Condensed Aromatic Hydrocarbon, $C_{20}H_{12}$. Roland Scholl, Christian Seer, and Richard Weitzenböck (*Ber.*, 1910, **43**, 2202—2209).—Scholl and Mansfeld (this vol., i, 494) have shown that *meso*-benzdianthrone, when heated at 140—145° with

anhydrous aluminium chloride, is converted into *meso*-naphthadianthrone. By the same reaction the hydrocarbon $C_{20}H_{12}$ (annexed formula) is obtained from 1 : 1′-dinaphthyl and also directly from naphthalene. To establish the constitution as a *peri*-derivative, 1 : 8-naphthalenediamine was converted into the azimide, this into *8-iodo-α-naphthylamine*, and further into 1 : 8-*di-iodonaphthalene*, which last when heated with copper powder yielded the above hydrocarbon, peri-*dinaphthalene*, which it is proposed to term perylene. *Perylene* forms glistening yellow or bronze-hued, crystalline plates, m. p. 264—265°, and gives yellow or reddish-yellow solutions with a brilliant blue fluorescence.

8-*Iodo-α-naphthylamine* forms colourless needles, m. p. 82°; the *hydrochloride* forms grey needles, which darken at 170°, m. p. 186—189° (decomp.). 1 : 8-Di-iodonaphthalene forms bright brown needles, m. p. 109°.

Dibenzoylperylene, prepared by the action of benzoyl chloride and aluminium chloride on perylene, was obtained in yellow crystals, m. p. 280—285°; the xylene solution shows a green fluorescence.

E. F. A.

Monoalkylnitroamines. Antoine P. N. Franchimont (*Rec. trav. chim.*, 1910, [ii], **14**, 296—312. Compare Abstr., 1898, i, 9).—Contrary to the observations of Simon Thomas (Abstr., 1891, 167), the author finds that picryl chloride in alcoholic solution reacts with the potassium salts of ethyl- and propyl-nitroamine, giving respectively trinitrophenyl-ethyl- and -propyl-nitroamines. The yield of trinitrophenylethylnitroamine amounts to almost 90% of theory, but in the second reaction only about two-thirds of the picryl chloride is decomposed, a mixture of almost equimolecular quantities of potassium chloride and picrate being precipitated, whilst the unattacked picryl chloride will react with a further amount of potassium propylnitroamine. Similarly, potassium butylnitroamine when treated with picryl chloride gives a small quantity of *trinitrophenylbutylnitroamine*, $C_4H_9{\cdot}N(NO_2){\cdot}C_6H_2(NO_2)_3$, which forms almost colourless, nacreous spangles, m. p. 98—99°, together with much potassium picrate.

This compound can also be prepared by van Romburgh's method (*Rec. trav. chim.*, 1883, **2**, 112), *trinitrophenylbutylamine*,

$$C_4H_9{\cdot}NH{\cdot}C_6H_2(NO_2)_3,$$

which crystallises in long, slender, orange-yellow needles, m. p. 80·5—81°, being an intermediate product.

The decreasing yield of aliphatic trinitrophenylnitroamine, obtained on ascending the series of aliphatic nitroamines, is probably due to the increasing degree of dissociation of the potassium salts of the latter, and thus supports Simon Thomas's conclusion that methylnitroamine has a more strongly acid character than that possessed by its homologues.

Attempts to prepare acetyl or benzoyl derivatives of methylnitroamine failed (compare Simon Thomas, *loc. cit.*). With benzoyl chloride alone, or in the presence of benzene, methylnitroamine gives nitrous oxide, methyl chloride, and benzoic acid. Addition of benzoyl chloride to a mixture of the silver derivative of methylnitroamine with sand causes a violent explosion. The reaction with benzoyl chloride is explicable on the assumption that methylnitroamine has the constitution

$$NMe{:}NO{\cdot}OH.$$

The nitroamine is perhaps transformed into the latter under the influence of substances with which it reacts, thus the salts of *o*- and *p*-nitrophenol and of carbonic, hydrocyanic, cyanic, sulphydric, sulphurous, and nitrous acids are decomposed by it, but it does not combine directly with aromatic amines, although it does so with ammonia. This constitution is also supported by the observation that methylnitroamine combines with piperidinomethyl alcohol and with piperazine. In the former case, large, colourless crystals, m. p. 52°, of *piperidinemethylnitroaminomethane*, $NO_2{\cdot}NMe{\cdot}CH_2{\cdot}C_5NH_{10}$, are produced. This compound is unstable, and dissolves slowly with decomposition in cold water. Butylnitroamine reacts with piperidinomethyl alcohol, giving a *liquid product*, whilst ethylenedinitroamine forms magnificent crystals, m. p. 123°, of *piperidine-ethylenedinitroaminomethane*, $C_2H_4[N(NO_2){\cdot}CH_2{\cdot}C_5NH_{10}]_2$, which behave similarly to the methyl derivative. With piperazine, methylnitroamine forms *piperazinedimethylenedinitroamine*,

$$NO_2{\cdot}NMe{\cdot}CH_2{\cdot}N<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>N{\cdot}CH_2{\cdot}NMe{\cdot}NO_2,$$

which crystallises in nacreous leaflets, decomposing at 170°.

The latter compounds react as though they possess the constitution $R{\cdot}N{:}NO{\cdot}OR'$; nevertheless, in previous communications (Abstr., 1899, i, 106), reactions in support of the formula $CH_3{\cdot}NH{\cdot}NO_2$ for methylnitroamine have been described. E. H.

Trinitrophenylalkylnitroamines. Antoine P. N. Franchimont (*Rec. trav. chim.*, 1910, [ii], **14**, 313—314).—The alkylpicramides, $C_6H_2(NO_2)_3{\cdot}NHR$, are yellow or orange-coloured substances, whilst the trinitrophenylalkylnitroamines are only very faint yellow, but are coloured purple-red by alkalis.

The author considers that the difference in colour between the two classes of compounds is related to the replacement of the imide hydrogen by the nitro-group, and points out that this is in accordance with the views recently expressed by Hantzsch (this vol., i, 475). The coloration of the trinitrophenylalkylnitroamines by alkalis is perhaps due to the conjugation of two nitro-groups with the metal or ammonia (compare Hantzsch and Picton, Abstr., 1909, i, 467).

E. H.

Homochromoisomerism. Max Busch (*Ber.*, 1910, **43**, 2070. Compare Hantzsch, this vol., i, 474).—Polemical. Busch and Pungs (Abstr., 1909, i, 564) were the first to recognise the two isomerides of picrylmethylaniline, and to carry out the mutual interconversion.

E. F. A.

Products of the Bromination of *o*- and *p*-Nitrophenol. Henri van Erp (*Rec. trav. chim.*, 1910, [ii], 14, 187—237).—The author has studied the preparation of 4-bromo-, 6-bromo- and 4 : 6-dibromo-2-nitrophenol, 2-bromo- and 2 : 6-dibromo-4-nitrophenol, 4-bromo-2 : 6-dinitrophenol, and 2-bromo-4 : 6-dinitrophenol. A résumé of the literature relative to each of these compounds is given. The following new compounds are described. *Calcium* 4-*bromo*-2-*nitrophenoxide*, $(C_6H_3O_3NBr)_2Ca,2H_2O$, forms a bright orange precipitate composed of microscopic needles; 4-*bromo*-2-*nitrophenyl acetate*, prepared from the phenol by means of acetic anhydride containing a small quantity of sulphuric acid, crystallises in very brilliant, colourless, triangular plates, m. p. 74·5—74·75°. By treating the product of the bromination of *o*-nitrophenol with aniline, the author separated a small quantity of 6-bromo-2-nitrophenol, which has not hitherto been prepared in this way. *Barium* 4 : 6-*dibromo*-2-*nitrophenoxide*, $(C_6H_2O_3NBr_2)_2Ba,2H_2O$, forms thin, doubly-refracting, orange needles; the *additive* compound of 4 : 6-dibromo-2-nitrophenol and aniline, $NO_2\cdot C_6H_3Br_2\cdot OH,NH_2Ph$, a crystalline, yellow powder, m. p. 87° (variable), easily breaks down into its components. If 4 : 6-dibromo-2-nitrophenol is left in contact with nitric acid (D 1·41) for some months, it is converted into 2-bromo-4 : 6-dinitrophenol, of which the *aniline* derivative has m. p. 151°. For 4-bromo-2 : 6-dinitrophenol the author finds m. p. 74·5°, whilst Körner (*Zeit. Chem.*, 1868, 4, 322) and Armstrong and Prevost (Trans., 1875, 28, 520; Abstr., 1874, 1164) give 78°, and Austen (*Jahresber*, 1878, i, 550) gives 71°.

Potassium 4-*bromo*-2 : 6-*dinitrophenoxide*, $C_6H_2O_5N_2BrK$, is a blood-red substance; the *sodium* salt, $C_6H_2O_5N_2BrNa,2H_2O$, forms thin, doubly-refracting needles of the same colour; the *barium* and *calcium* salts, $(C_6H_2O_5N_2Br)_2Ca,2H_2O$, crystallise in bright yellow needles. The *additive* compound of 4-bromo-2 : 6-dinitrophenol and aniline, $C_6H_3O_5N_2Br,PhNH_2$, is an orange, microcrystalline powder, m. p. 137·5—137·75°, sufficiently stable to be recrystallised from warm water; 4-*bromo*-2 : 6-*dinitrophenyl acetate* crystallises in brilliant doubly-refracting, colourless, orthorhombic prisms, m. p. 110·5°, which become yellowish-brown in moist air.

By the bromination of *p*-nitrophenol, previous workers have obtained 2-bromo-4-nitrophenol with too low a m. p. (102°). This is shown to be due to admixture with dibromonitrophenol, which cannot be removed by recrystallisation of the phenol or of its barium or potassium salt. By treating the benzene solution of the bromination product with aniline, the dibromonitrophenol is precipitated in the form of its aniline derivative. Pure 2-bromo-4-nitrophenol can be obtained from the filtrate in crystals, m. p. 112·25°. The presence of hydrobromic acid inhibits the formation of the dibromo-compound to a certain extent. *Sodium* 2-*bromo*-4-*nitrophenoxide*,

$$C_6H_3O_3NBrNa,2H_2O,$$

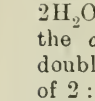
and the *potassium* salt ($1\frac{1}{2}H_2O$) crystallise in radial groups of microscopic, bright yellow, doubly-refracting, pointed needles; the *calcium* salt forms a microcrystalline powder composed of thin needles; the *additive* compound of 2-bromo-4-nitrophenol and aniline,

$$C_6H_4O_3NBr,NH_2Ph,$$

forms greenish-yellow crystals, m. p. 55—69°, which lose aniline

completely when exposed over sulphuric acid in a vacuum ; *2-bromo-4-nitrophenyl acetate* crystallises in irregular, birefracting, colourless prisms, m. p. 61·75°. For 2 : 6-dibromo-4-nitrophenol the author observed the m. p. 143°, and, contrary to the statements of previous workers, found that it was not decomposed at 180°. *Sodium* 2 : 6-*dibromo-4-nitrophenoxide*, $C_6H_2O_3NBr_2Na$, crystallises above 50° with $2H_2O$ in deep orange crystals, and below 20° with $5H_2O$ in yellow crystals; the *calcium* salt, $(C_6H_2O_3NBr_2)_2Ca,4H_2O$, crystallises in irregular, doubly-refracting, orange-coloured rhombs ; the *additive* compound of 2 : 6-dibromo-4-nitrophenol and aniline, $C_6H_3O_3NBr_2,NH_2Ph$, forms slender, yellow needles, m. p. 155·5°, which give almost colourless solutions in neutral solvents and only lose aniline very slowly when boiled with water. *Potassium* 2-*bromo*-4 : 6-*dinitrophenoxide* crystallises with $1H_2O$; the *additive* compound of 2-bromo-4 : 6-dinitrophenol and aniline, $C_6H_3O_5N_2Br,NH_2Ph$, forms slender, yellow needles, m. p. 151°, and can be recrystallised from boiling water ; *2-bromo-4 : 6-dinitrophenyl acetate* forms short, stout, doubly-refracting, colourless, rhombohedric crystals, m. p. 104·5° E. H.

Catecholmonosulphonic Acid. Curt Gentsch (*Ber.*, 1910, **43**, 2018—2020).—Cousin (Abstr., 1893, i, 637) considered the catecholsulphonic acid, which he obtained by sulphonating catechol below 100°, to be an ortho-acid of constitution (I), and isomeric with the para-acid (II) described by Barth (Abstr., 1879, 933).


(I.)


(II.)

It is shown that the two acids are identical, both forming a characteristic barium salt ($4H_2O$) crystallising in rosettes of rectangular prisms, whilst Cousin's acid gives 1 : 2-dimethoxybenzene-4-sulphonic acid (compare Paul, Abstr., 1906, i, 843) on methylation. It must accordingly be removed from the literature. E. F. A.

Simple Formation of Benzyl Ethers. Hans von Halban (*Ber.*, 1910, **43**, 2071. Compare Braun, this vol., i, 479).—Polemical. The fact that benzyl halogenides react with alcohol, forming ethers, has already been observed (compare Abstr., 1909, ii, 722). Benzyl halogenides also react with phenols and carboxylic acids.

E. F. A.

Preparation of Aromatic Alcohols and their Acetates. Alfred Wohl and Erich Berthold (*Ber.*, 1910, **43**, 2175—2185).—Grignard (Abstr., 1904, i, 494) has described the preparation of phenylethyl alcohol by the following series of reactions :

$$CH_2Br\cdot CH_2Br \longrightarrow CH_2Br\cdot CH_2\cdot OPh,$$

$$CH_2Ph\cdot CH_2\cdot OPh \longrightarrow CH_2Ph\cdot CH_2Br \longrightarrow CH_2Ph\cdot CH_2\cdot OH,$$

and the authors have re-examined these reactions in detail. A 59% yield of pure ω-bromophenetole can be obtained by gradually adding 4*N*-sodium hydroxide solution to a mixture of ethylene dibromide, phenol, and water heated in an oil-bath at 100—105°, and kept well stirred. A 48·4% of ω-chlorophenetole can be obtained by a similar method, using ethylene dichloride, a shaking apparatus, and a tem-

perature of 110°. β-Naphthol gives a 40% yield of its ω-bromoethyl ether (Kolbe, Abstr., 1881, 177). Eugenole gives a 25% yield of the *bromoethyl ether*, $CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}CH_2Br$, which has m. p. 26—27° and b. p. 160—170°/7 mm.

Guaiacol ω-bromoethyl ether, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2Br$ (40% yield), has m. p. 43—45° and b. p. 135—140°/7 mm.

Phenyl vinyl ether, $CH_2{:}CH{\cdot}OPh$, obtained by heating ω-bromophenetole with twice its weight of anhydrous potassium hydroxide in a copper flask, is a colourless liquid, b. p. 155—156°. A by-product is *diphenoxyethyl ether*, $O(CH_2{\cdot}CH_2{\cdot}OPh)_2$, which crystallises from dilute alcohol in colourless needles, m. p. 66—67°. *Eugenyl vinyl ether*, $CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{:}CH_2$ (50% yield), is a mobile liquid, b. p. 260—262°, and *guaiacyl vinyl ether* (50% yield) has b. p. 202—203°.

ω-Bromophenetole, bromobenzene, and sodium powder in the presence of ether yield phenol, ethylene, and unaltered bromobenzene.

A 71% yield of ω-phenylphenetole is obtained by the action of magnesium phenyl bromide on ω-bromophenetole in the presence of xylene at 150—155°, and when this is boiled with glacial acetic acid and 70% sulphuric acid, a 65% yield of phenylethyl acetate is obtained.

A 38% yield of phenylethyl alcohol can be obtained by the action of nitrous acid on β-phenylethylamine.

Phenylmethylvinyl acetate, $CMePh{:}CH{\cdot}OAc$, obtained by boiling hydratropaldehyde with acetic anhydride and two drops of concentrated sulphuric acid, is a clear, colourless liquid, b. p. 120—122°/8—9 mm., and when reduced with hydrogen and platinum black yields *β-phenylpropyl acetate*, $CHMePh{\cdot}CH_2{\cdot}OAc$, with b. p. 103—105°/10 mm.

J. J. S.

Fixation of Trioxymethylene by Magnesium Derivatives of the Homologues of Benzyl Bromide. Paul Carré (*Compt. rend.*, 1910, 151, 149—151.* Compare Abstr., 1909, i, 544).—Trioxymethylene reacts with magnesium mesityl bromide in the same way as with magnesium benzyl chloride (Tiffeneau, Abstr., 1904, i, 48), forming *s*-mesitylcarbinol, $C_6H_3Me_2{\cdot}CH_2{\cdot}OH$, needles, m. p. 88—89°, b. p. 140—141°/15 mm.; the *phenylurethane* crystallises in long prisms, m. p. 124—125°. The product of the reaction also contains *s*-dixylylethane (Moritz, Abstr., 1899, i, 910), mesitylene, and *s-dixylyldimethyl ether*, $O(CH_2{\cdot}C_6H_2Me_2)_2$, silky needles, m. p. 148°. The constitution of the latter follows from its conversion by hydrogen bromide into 2:4:6-*trimethylbenzyl bromide*, $C_6H_2Me_3{\cdot}CH_2Br$, long tablets, m. p. 52°, which yield *s*-mesitylcarbinol on hydrolysis.

Wispek's *s*-xylylacetic acid has m. p. 103° (Abstr., 1883, 1095); it could not be detected amongst the products of the foregoing reaction. The *ethyl* ester has b. p. 141—142°/18 mm., and on reduction forms *s-xylylethanol*, a mobile liquid having a rose-like odour, b. p. 134—135°/15 mm.; the *phenylurethane* crystallises in long prisms, m. p. 99°; the *acetate* has b. p. 138—139°/13 mm.

W. O. W.

Crystalline Form of Cholesteryl Salicylate. Ettore Artini (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 782—784).—Cholesteryl

* and *Bull. Soc. chim.*, 1910, [iv], 7, 841—846.

salicylate, $OH{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_{27}H_{45}$, prepared by fusing cholesterol and salicylic acid at 170°, melts at 180°, and has $[\alpha]_D^5 - 53{\cdot}78°$ in chloroform solution. The crystals are small, but distinctly formed, and are triclinic [$a:b:c = 0{\cdot}77364:1:0{\cdot}50407$; $a = 92°55'24''$, $\beta = 101°58'32''$, $\gamma = 95°14'10''$]. C. H. D.

pp-Dibromobenzhydrol. A Correction. Heinrich Biltz (*Ber.*, 1910, **43**, 2262. Compare this vol., i, 570).—The compound, m. p. 174—175°, obtained by the decomposition of dibromobenzilic acid, and described as dibromobenzhydrol, is in reality di-*p*-bromobenzophenone. E. F. A.

Condensation of Ethyl Nitrate with *o*-Bromophenylacetonitrile. Wilhelm Wislicenus and Max Fischer (*Ber.*, 1910, **43**, 2234—2243).—Ethyl nitrate condenses with *o*-bromophenylacetonitrile in presence of sodium ethoxide less readily than with the corresponding *p*-compound (Abstr., 1909, i, 29). In presence of potassium ethoxide the *potassium* salt of o-*bromo*-α-iso*nitrophenylacetonitrile*, $C_6H_4Br{\cdot}C(CN){:}NO_2K$, is obtained. Nitrous acid is readily eliminated from the free compound to form oo′-*dibromo*-αα′-*dicyanostilbene*. The *iso*nitro-group is more stable in alkaline solution; on boiling, cyanide is eliminated and o-*bromo*-ω-*nitrotoluene* formed. Stronger heating causes the elimination of the oximino-group also, and oo′-*dibromostilbene* is obtained. Sodium hydroxide and hydrogen peroxide convert the cyano-group into carbonamide. Treatment with bromine and subsequent elimination of nitric oxide and bromine leads to *o*-bromophenylacetonitrile. On reduction, *o*-bromo-α-aminophenylacetic acid is obtained.

o-Bromophenylacetonitrile boils without decomp. at 145—147°/13 mm.

Sodium o-*bromo*-α-iso*nitrophenylacetonitrile* crystallises in colourless plates, m. p. 283—285° (decomp.), and explodes on further heating. The *potassium* salt forms colourless, glistening plates. Both salts dissolve in water with a neutral reaction, the solution having a sweet taste. It gives neither coloration nor precipitate with ferric chloride, but the alcoholic solution becomes a deep brownish-red with this reagent.

The free o-*bromo*-α-iso*nitrophenylacetonitrile* forms faintly yellow-coloured, pyramidal prisms, m. p. 51—52°, and gives an intense red coloration with ferric chloride in alcoholic solution. The *methyl ether* is colourless, m. p. 104—105°.

oo′-*Dibromo*-αα′-*dicyanostilbene*, $[C_6H_4Br{\cdot}C(CN){:}]_2$, crystallises in colourless needles, m. p. 145°.

o-*Bromo*-ω-*nitrotoluene* crystallises in colourless needles, m. p. 55—56°, and shows no ferric chloride reaction.

oo′-*Dibromostilbene* is obtained in colourless, lustrous plates, m. p. 206—208°; the *dibromide* forms colourless needles, m. p. 225°.

o-Bromophenylacetonitrile was obtained in almost colourless, long, flat, glistening needles, m. p. 65—67° (Russanoff: 62—64°). It reacts in ethereal solution with phenylhydrazine, forming o-*bromobenzophenylhydrazide*, which crystallises in needles, m. p. 190—198°.

o-*Bromo-α-aminophenylacetic acid*, $C_6H_4Br\cdot CH(NH_2)\cdot CO_2H$, separates in leaflets, which sublime at 220—225°, m. p. 221° (in closed tube).

The *potassium* salt of o-*bromo*-α-iso*nitrophenylacetamide*,

$$C_6H_4Br\cdot C(CO\cdot NH_2):NO_2K,$$

crystallises in long, faintly yellow-coloured needles, decomp. 240°. On treatment with bromine, α:o-*dibromo-α-nitrophenylacetamide* is produced in colourless, microscopic prisms, m. p. 156—157° (decomp.).

E. F. A.

Action of Benzaldehyde on the Monosodium Derivative of Phenylacetonitrile. F. Bodroux and Felix Taboury (*Bull. Soc. chim.*, 1910, [iv], 7, 735—736).—When the monosodium derivative of phenylacetonitrile in ethereal solution is treated with benzaldehyde, the product consists of a mixture of substances. From the latter the only definite compound that can be isolated is α-phenylcinnamonitrile, $CHPh:CPh\cdot CN$, already described by Meyer, Janssen, Neure, and Frost (Abstr., 1889, 596, 597).

The nitrile is probably formed by the reactions: $Ph\cdot CHO + Ph\cdot CHNa\cdot CN = Ph\cdot CH(ONa)\cdot CHPh\cdot CN$; $Ph\cdot CH(ONa)\cdot CHPh\cdot CN = NaOH + CHPh:CPh\cdot CN$. Sodium benzoate, formed probably by a secondary reaction, is found in the aqueous liquor from which the above crude product is separated. E. H.

The Walden Inversion. V. Optically Active β-Amino-β-phenylpropionic Acid. Emil Fischer, Helmuth Scheibler, and Reinhart Groh (*Ber.*, 1910, 43, 2020—2030. Compare Abstr., 1909, i, 359).—The formyl compound of β-amino-β-phenylpropionic acid has been resolved by means of quinidine and quinine into the optically active forms. By treatment with nitrous acid, these were converted into the corresponding hydroxy-acids, but the change is accompanied by racemisation, due to the influence of the direct attachment of the phenyl to the asymmetric carbon atom. Enough activity remains, however, to identify the hydroxy-acids with those obtained by McKenzie and Humphries (Trans., 1910, 97, 121). *d*-β-Amino-β-phenylpropionic acid gives *l*-β-hydroxy-β-phenylpropionic acid. In the case of the ethyl ester of the amino-acid, the racemisation is less, and the hydroxy-acid rotates in the same direction, so that no Walden change takes place.

dl-β-*Formylamino-β-phenylpropionic acid*,

$$CHO\cdot NH\cdot CHPh\cdot CH_2\cdot CO_2H,$$

forms large, colourless prisms, which soften at 125°, m. p. 128—129° (corr.), to a colourless liquid. By means of the *quinidine* salt, d-β-*formylamino-β-phenylpropionic acid* was obtained in aggregates of microscopic, short needles, which soften at 138°, m. p. 142—143°, $[\alpha]_D^{20}$ +116·4° (±0·2°). The *quinine* salt yields the corresponding *l*-isomeride, which is very similar; $[\alpha]_D^{20}$ −114·4° (±0·2°). d-β-*Amino-β-phenylpropionic acid*, obtained by heating the formyl compound with 10% hydrochloric acid, crystallises in stout plates, m. p. 234—235° (decomp.), and has $[\alpha]_D^{20}$ +6·9° in water, −1·3° in *N*-hydrochloric acid, −9·1° in *N*-sodium hydroxide. The l-*isomeride* is precisely similar in crystalline form, and has $[\alpha]_D^{25}$ −7·5° in water, +1·3° in *N*-hydrochloric acid, +8·9° in *N*-sodium hydroxide. The copper salt crystallises in plates.

Ethyl d-*β-amino-β-phenylpropionate* is a viscid oil, b. p. 155° (corr.)/13 mm., D_4^{24} 1·063, $[\alpha]_D^{24}$ + 13·74° (± 0·02°). The *l*-isomeride was prepared from partially racemised material, and had $[\alpha]_D^{20}$ − 8·09° (± 0·04°).

Conversion of the *d-β*-aminophenylpropionic acid into the hydroxy-acid gave a product, m. p. 96—98°; $[\alpha]_D^{25}$ − 3·3°, whereas McKenzie and Humphries (*loc. cit.*) found $[\alpha]_D^{20}$ − 18·9°. Similarly, the *l*-acid yields an hydroxy-acid; m. p. 94—95°; $[\alpha]_D^{26}$ + 3·2°.

Ethyl *d-β*-aminophenylpropionate yields the hydroxy-acid; $[\alpha]_D^{22}$ − 3·5°, rising to − 6·4° on crystallisation. E. F. A.

Action of Esters of Monobasic Aliphatic Acids on the Sodium Derivative of Phenylacetonitrile. F. Bodroux (*Compt. rend.*, 1910, **151**, 234—236.* Compare Walther and Schickler, Abstr., 1897, i, 522).—Sodamide was added to phenylacetonitrile dissolved in dry ether, and an alkyl ester added to the resulting sodium derivative. The following compounds were prepared in this way: *α-Cyanophenylacetaldehyde*, CN·CHPh·CHO, m. p. 157—158°, from ethyl formate, which on benzoylation gave Walther's enolic benzoyl derivative, m. p. 119°. Amyl formate gave the same compound in diminished yield (50%). Ethyl acetate formed *α-cyanobenzyl methyl ketone*, CN·CHPh·COMe, large prisms, m. p. 90°. α-Cyano-α-phenylbutan-*β*-one has m. p. 73° (Walther and Schickler give m. p. 58°). The foregoing compounds are easily hydrolysed by dilute alkalis, regenerating phenylacetonitrile.

W. O. W.

Tetrahydroellagic Acid. Maximilian Nierenstein (*Ber.*, 1910, **43**, 2016—2017. Compare this vol., i, 389).—The tetrahydroellagic acid described by Oser and Böker (Abstr., 1880, 394), crystallising from pyridine in small, yellow needles, is in reality ellagic acid.

The isomeric tetrahydroellagic acid of Oser and Kalmann (Abstr., 1881, 815), obtained in small, silky needles by fusing ellagic acid with potassium hydroxide, is in reality pentahydroxydiphenylmethylolide, $C_{13}H_8O_7$. E. F. A.

The Beckmann Rearrangement. Pieter J. Montagne (*Ber.*, 1910, **43**, 2014—2016).—Schroeter (Abstr., 1909, i, 617) has explained the Beckmann rearrangement on the assumption of the formation of an additive product with hydrogen chloride, and the conversion of this into a compound with a univalent nitrogen atom, $R_2CCl{\cdot}N<$. It is pointed out that in the case of the ketoximes, RR'C:N·OH, the additive product and the unsaturated compound cannot be intermediate compounds. Wallach (Abstr., 1906, i, 522) has assumed the elimination and subsequent addition of hydrogen chloride. If this were so, the benzene nucleus, after the rearrangement, must be combined with a different carbon atom than before, which was shown not to be the case (compare Montagne, Abstr., 1907, i, 140, 854). E. F. A.

Isomerism and Polymorphism. I. Ketones of the Type of Benzylidenedeoxybenzoin and their Interconversion by Heat, Light, and Other Agencies. Hans Stobbe and Forsyth J. Wilson (*Annalen*, 1910, **374**, 237—287).—The isomerism of the benzylidene-

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 848—852.

deoxybenzoins described by Stobbe and Niedenzu (Abstr., 1902, i, 103) has been more thoroughly studied in the cases of the ketones obtained from the three nitrobenzaldehydes and from piperonal.

Hydrogen chloride is passed for six hours into an ethereal solution of deoxybenzoin and *o*-nitrobenzaldehyde at 0°; after being kept for three days at this temperature, the solution deposits white and yellow crystals. The former, after recrystallisation from benzene, have m. p. 132—133°, and consist of *chloro*-o-*nitrobenzyldeoxybenzoin*, $NO_2 \cdot C_6H_4 \cdot CHCl \cdot CHPh \cdot COPh$, which is an unstable substance, being converted into the *ether*, $NO_2 \cdot C_6H_4 \cdot CH(OEt) \cdot CHPh \cdot COPh$, m. p. 128—129°, by boiling alcohol, and losing hydrogen chloride by keeping in the air or in benzene or ethereal solution, or, best, by heating with aniline, yielding the yellow crystals, which consist of o-*nitrobenzylidenedeoxybenzoin*, $NO_2 \cdot C_6H_4 \cdot CH:CPh \cdot COPh$, m. p. 120—121°. This unsaturated ketone is converted into a paler yellow isomeride, iso-o-*nitrobenzylidenedeoxybenzoin*, m. p. 109—110°, by an exposure to sunlight for three months of its benzene solution containing a little iodine, by passing hydrogen chloride into its benzene solution for a few minutes, and then keeping for eleven hours, or by the action of sunlight on the powdered crystals; in each case a mixture of the two isomerides is produced, which is separated by means of alcohol. The *iso*-compound is more easily converted into the other, the change proceeding to the extent of 50% by exposing its benzene solution containing iodine to sunlight for five days, or by keeping its benzene solution, containing hydrogen chloride, for a week. Both isomerides have the same molecular weight, and yield the same o-*nitrobenzamarone*, $NO_2 \cdot C_6H_4 \cdot CH(CHPh \cdot COPh)_2$, m. p. 237—238°, when their alcoholic solutions are boiled with an equal molecular quantity of deoxybenzoin and a little sodium ethoxide; their alcoholic solutions, however, give different ultraviolet absorption spectra.

When an ethereal mixture of deoxybenzoin and *p*-nitrobenzaldehyde is treated with hydrogen chloride at 0°, and is kept for eleven days, a mixture is obtained, consisting chiefly of stout, yellow prisms of iso-p-*nitrobenzylidenedeoxybenzoin*, m. p. 164—165°, together with smaller amounts of elongated, yellow prisms of allo-p-*nitrobenzylidenedeoxybenzoin*, m. p. 148—149°, and white crystals of *chloro*-p-*nitrobenzyldeoxybenzoin*, $NO_2 \cdot C_6H_4 \cdot CHCl \cdot CHPh \cdot COPh$, m. p. 157—158°, the three substances being separated by fractional crystallisation from alcohol; the last-mentioned compound is converted into a mixture of the other two by boiling 50% potassium hydroxide.

p-*Nitrobenzylidenedeoxybenzoin*, m. p. 133·5—135·5°, which crystallises in yellow prisms, is produced when a benzene solution (containing iodine) of the *iso*-compound is boiled for twelve hours in diffuse daylight. *p*-Nitrobenzylidenedeoxybenzoin and the *iso*- and *allo*-isomerides all have the same molecular weight, yield the same *dibromide*, $NO_2 \cdot C_6H_4 \cdot CHBr \cdot CBrPh \cdot COPh$, decomposing at 156—157°, with bromine in carbon tetrachloride, produce the same p-*nitrobenzamarone*, m. p. 236—237°, and any one is converted into a mixture of the three by (i) exposing its benzene solution, containing iodine, to sunlight for four months, (ii) boiling the same solution for twelve hours in diffuse sunlight,

(iii) keeping its benzene solution, containing hydrogen chloride, for a week. All three give different absorption spectra in alcohol, and also their solutions in concentrated sulphuric acid, or in trichloroacetic acid, are colorimetrically different. A benzene or alcoholic solution of any one, even after being boiled, deposits, on cooling, only crystals of the ketone originally dissolved, even after inoculation with a crystal of either of the other two isomerides. When fused and cooled immediately, any one of the three isomerides resolidifies unchanged, but if kept in the molten condition for only five minutes a change occurs, and a mixture of the three ketones is formed.

The action of hydrogen chloride on an ethereal solution of deoxybenzoin and *m*-nitrobenzaldehyde at 0° leads, after three days, to the formation of a white precipitate, consisting of two stereoisomeric (?) modifications of *α-chloro*-m-*nitrobenzyldeoxybenzoin*,

$$NO_2 \cdot C_6H_4 \cdot CHCl \cdot CHPh \cdot COPh,$$

which are separated by crystallisation from benzene; one form crystallises in white needles, m. p. 181—182°, the other in stout, white crystals, m. p. 192—193°. When boiled with potassium hydroxide the latter yields m-*nitrobenzylidenedeoxybenzoin*, m. p. 85·5—86·5°, crystallising in white needles, whilst the former yields a mixture of *m*-nitrobenzylidenedeoxybenzoin and iso-m-*nitrobenzylidenedeoxybenzoin*, yellow prisms, m. p. 86·5—87·5°, the two being separated by crystallisation, first from ethyl acetate, and then from alcohol. *m*-Nitrobenzylidenedeoxybenzoin crystallises unchanged from boiling solutions; the *iso*-compound, however, is partly converted into allo-m-*nitrobenzylidenedeoxybenzoin*, m. p. 94·5—95·5°, which crystallises in white prisms. All three isomerides have the same molecular weight, form the same *dibromide*, decomposing at 159—161°, and the same m-*nitrobenzamarone*, m. p. 220—221°, and are mutually interconvertible by boiling their solutions in benzene, containing iodine, in diffuse daylight, by keeping their benzene solutions, containing hydrogen chloride, for a week, or by heating at 160°; by each method a mixture of the three isomerides is produced from any one. The *iso*- and the *allo*-isomerides show almost identical behaviour, giving the same absorption spectra in alcohol, different from that of *m*-nitrobenzylidenedeoxybenzoin, and solutions in concentrated sulphuric acid or trichloroacetic acid, which are colorimetrically the same. Solutions of the *iso*- or of the *allo*-isomeride in any solvent deposit mixtures of both, whilst *m*-nitrobenzylidenedeoxybenzoin alone separates from its solutions, even after inoculation with a crystal of either of the other two isomerides. All three melt and resolidify to the original substance if cooled at once, but when kept in a state of fusion for five minutes, *m*-nitrobenzylidenedeoxybenzoin changes to a mixture of the *iso*- and the *allo*-isomerides, *iso-m*-nitrobenzylidenedeoxybenzoin resolidifies unchanged, whilst the *allo*-isomeride partly changes into *m*-nitrobenzylidenedeoxybenzoin. When slowly heated, a mixture of equal parts of *m*-nitrobenzylidenedeoxybenzoin and the *iso*- or *allo*-isomeride fuses at a temperature below the m. p. of either constituent, whilst mixtures of the *iso*- and the *allo*-isomerides have the same m. p. as the *allo*-isomeride.

The action of hydrogen chloride on ethereal piperonal and deoxy-

benzoin at 0° leads, after twelve hours, to the production of a yellow mass, from which *chloropiperonyldeoxybenzoin*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CHCl{\cdot}CHPh{\cdot}COPh,$$

m. p. 167—168° (decomp.), is obtained in colourless crystals by crystallisation from benzene. The substance is converted into the *ethyl ether*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH(OEt){\cdot}CHPh{\cdot}COPh$, m. p. 114—115°, by boiling ethyl alcohol, into the corresponding *methyl ether*, m. p. 119—120°, by boiling methyl alcohol, and by boiling water into a mixture of *piperonylidenedeoxybenzoin*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CPh{\cdot}COPh$, m. p. 128—129°, crystallising in white prisms, and iso*piperonylidenedeoxybenzoin*, m. p. 119—120°, crystallising in yellow prisms. The two isomerides give different absorption spectra. They can be recrystallised unchanged from solvents of low b. p., but either is converted into a mixture of the two by boiling its solution in benzene, containing iodine, in diffused daylight, or by the exposure of the same solution to sunlight at the ordinary temperature.

The nature of the isomerism described above is discussed at some length. There is no doubt that the *iso*- and the *allo*-isomerides resemble each other much more closely than the ketones with unprefixed names. The last and the *iso*-isomerides are most probably *syn*- and *anti*-stereoisomerides. The *iso*- and the *allo*-isomerides undoubtedly differ from each other in solution and in the fused state; they are, therefore, true chemical isomerides, for the representation of which the ordinary formulæ do not suffice. C. S.

Ring Formation from the Ketonic Acids. Edmond E. Blaise and A. Koehler (*Bull. Soc. chim.*, 1910, [iv], 7, 710—721).—It has been shown previously (Vorländer, Abstr., 1897, i, 272; Blaise and Maire, Abstr., 1908, i, 390) that the δ-ketonic acids are condensed by sodium ethoxide to form derivatives of dihydroresorcinol.

The object of the present work was to determine whether this property persists in the ϵ-, ζ-, and η-ketonic acids, in which the carbonyl group is farther removed from the carboxyl group in the molecule, and if so, the manner in which the ring-formation is effected.

The esters of the ϵ-ketonic acids under the above conditions are transformed into 2-acyl*cyclo*pentanones. The fact that the product of the condensation of ethyl ω-acetyl-*n*-valerate contains only one hydrogen atom replaceable by alkyl groups, shows that a hepta-methylene derivative is not formed according to such a scheme as $\begin{matrix}CH_2{\cdot}CH_2{\cdot}CO{\cdot}OEt\\ |\\ CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3\end{matrix} = \begin{matrix}CH_2{\cdot}CH_2{\cdot}CO\\ |\\ CH_2{\cdot}CH_2{\cdot}CO\end{matrix}\!\!>\!CH_2 + EtOH$, and therefore that the reaction differs from that undergone by the δ-ketonic acids. The 2-acyl*cyclo*pentanones, being β-diketones, contain a hydrogen atom replaceable by sodium, the derivatives so formed being readily alkylated. Special precautions, however, are necessary in carrying out this alkylation, otherwise the closed carbon chain is ruptured by the action of the sodium ethoxide. The 2-acyl-2-alkyl*cyclo*pentanones are readily hydrolysed by alkalis, giving δ-alkyl-ϵ-ketonic acids.

The esters of the ζ-ketonic acids are similarly condensed by sodium

ethoxide, giving 2-alkyl*cyclo*hexanone, not octandione, derivatives, whilst the η-ketonic acids do not undergo ring-formation. The conclusion is drawn that compounds containing more than six carbon atoms in a closed chain cannot be produced by reactions of this kind.

2-Propionyl*cyclo*pentanone, $\begin{array}{l} CH_2\cdot CH(COEt) \\ CH_2\cdot CH_2 \end{array} > CO$ (Abstr., 1909, i, 479), gives a violet coloration with ferric chloride; the *copper* salt forms grey leaflets; the *magnesium* salt, needles, m. p. 113—114° (decomp.), which contain $2H_2O$; the *pyrazole* crystallises in hexagonal prisms, m. p. 119°; in acetic acid it has a molecular weight corresponding with the formula $C_8H_{12}N_2$, but in benzene the molecular weight agrees with that of the azine, $C_{16}H_{24}N_4$; the *disemicarbazone* forms a crystalline powder, m. p. 236°.

2-*Propionyl*-2-*methyl*cyclo*pentanone* is a colourless liquid, b. p. 94—96°/12 mm. It gives no coloration with ferric chloride. 2-*Propionyl*-2-*ethyl*cyclo*pentanone* has b. p. 107—108°/12 mm. It gives no coloration with ferric chloride. δ-*Propionyl*-n-*hexoic acid*,

$$COEt\cdot CHMe\cdot[CH_2]_3\cdot CO_2H,$$

is a colourless liquid, b. p. 164°/10 mm.; the *semicarbazone* has m. p. 139·5°. δ-*Propionyl*-n-*heptoic acid*, $CH_2Me\cdot CH(COEt)\cdot[CH_2]_3\cdot CO_2H$, is a colourless liquid, b. p. 177°/11 mm.; the *semicarbazone* forms a white powder, m. p. 158—159°; the p-*nitrophenylhydrazone* forms canary-yellow crystals, m. p. 73° (rapid heating), 83—84° (slow heating); the *ethyl* ester has b. p. 136°/11 mm.

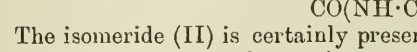
2-Propionyl*cyclo*hexanone (Abstr., 1909, i, 479) is a colourless liquid, having an agreeable odour resembling that of acetophenone; the *copper* salt forms small, greenish-grey crystals; the *carbamido-pyrazole*, $\begin{array}{l} CH_2\cdot CH_2\cdot C\text{———}CEt \\ CH_2\cdot CH_2\cdot C\cdot N(CO\cdot NH_2) \end{array} > N$ or

$$\begin{array}{l} CH_2\cdot CH_2\cdot C{:}CEt \\ CH_2\cdot CH_2\cdot C{=\!=}N \end{array} > N\cdot CO\cdot NH_2,$$

magnificent prisms, m. p. 126—127° (very rapid heating), 118° (slow heating), is formed under the conditions which give rise to the disemicarbazone in the case of the *cyclo*pentanone. When treated with sodium ethoxide and an alkyl iodide, 2-propionyl*cyclo*hexanone gives an inseparable mixture of aliphatic esters. E. H.

Constitution of Fenchone. III. LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 736—740).—It has already been shown (Abstr., 1908, i, 193) that when di*apo*fenchylcarbamide, $CO(NH\cdot C_9H_{17})_2$, is heated with 40% sulphuric acid, an unsaturated hydrocarbon, *apo*fenchene, C_9H_{16}, is formed. An attempt was made to characterise this hydrocarbon by preparing crystalline derivatives, but the additive compounds with hydrogen chloride and bromide and with nitrosyl chloride are liquids. From the product of the action of the nitrosochloride on piperidine, a trace of a *substance*, m. p. 175·5°, which is possibly the nitrolpiperidide, can be isolated. From the fact that, contrary to the original statement, the optical rotatory

power of the hydrocarbon is not constant, the authors conclude that *apo*fenchene is a mixture of the three hydrocarbons:



(I.) (II.) (III.)

which are the possible products of decomposition of the amide

$$CO(NH\cdot C_9H_{17})_2.$$

The isomeride (II) is certainly present to a considerable extent, (I) is probably present, and the mixture perhaps contains a small quantity of the (III) isomeride. The objection raised by Schimmel & Co. that a molecular transposition may have occurred during the reaction with sulphuric acid is controverted by the observation that the same hydrocarbon (b. p. 143°) is obtained by the action of nitrous acid on dihydrofencholenamide, $C_9H_{17}\cdot CO\cdot NH_2$.

When an alcoholic solution of *apo*fenchene is saturated with hydrogen chloride, the *hydrochloride*, $C_9H_{17}Cl$, is formed. It is a colourless, agreeably smelling liquid, b. p. 60°/8 mm., D_0^4 0·941, D_0^{18} 0·927, α_D +1·24°. The *hydrobromide*, prepared similarly, is a very unstable substance, b. p. 83°/13 mm., losing hydrogen bromide and becoming black very readily. It is reduced by magnesium to *apo*fenchene. E. H.

Sesquiterpene Alcohols. H. Kimura (*Ber. Deut. pharm. Ges.*, 1910, **20**, 293—297).—The author has shown previously that liquid *iso*cryptomeriol, by conversion into its xanthate and subsequent decomposition of the ester, is changed into solid cryptomeriol (this vol., i, 53). By similar treatment, cedrol is changed into its solid form, m. p. 86°, but santalol remains liquid, although its rotation is changed from −17°15′ to −5°. Also, the solid form of cedrol is obtained when the alcohol or its potassium derivative is distilled with superheated steam and the distillate is kept for several weeks.

C. S.

Oil of Savin. Fritz Elze (*Chem. Zeit.*, 1910, **34**, 767—768).—A product can be isolated from oil of savin which is easily soluble in dilute alcohol, and has a more intense odour than the original oil. It has D_{15} 0·960, and α_{100} +68°. On saponification with alcoholic potassium hydroxide and fractional distillation under diminished pressure of the product obtained by steam distillation, sabinol,

$$C_{10}H_{15}\cdot OH,$$

was obtained (D_{15} 0·950 and α_{100} +6°). The acetate prepared from this sabinol had D_{15} 0·972, α_{100} +79°, and b. p. 81—82°/3 mm. The original oil thus consisted mainly of sabinol acetate, about 83%.

The following products were also isolated in the fractional distillation: *n*-decaldehyde, geraniol, and dihydrocuminyl alcohol.

T. S. P.

Curcumin. J. Miłobędzka, Stanislaus von Kostanecki, and Victor Lampe (*Ber.*, 1910, **43**, 2163—2170).—Various hydroxychalkones have been synthesised in order to compare them with

curcumin. They resemble this compound, but do not dye unmordanted cotton. Vanillin condenses but slowly with pæonol, yielding 2′ : 4-*dihydroxy*-4′ : 3-*dimethoxychalkone*,

$$OMe\cdot C_6H_3(OH)\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)\cdot OH,$$

which crystallises from alcohol in yellow needles, m. p. 142—143°. The *diacetyl* derivative, $C_{21}H_{20}O_7$, forms yellow prisms, m. p. 155°. 2′ : 4-*Dihydroxy*-5′ : 3-*dimethoxychalkone*, $C_{17}H_{16}O_5$, prepared from vanillin and quinacetophenone monomethyl ether, crystallises from alcohol in orange-coloured plates, m. p. 122—123°. 4-*Hydroxy*-3-*methoxystyryl* 1-*hydroxynaphthyl* 2-*ketone*,

$$OH\cdot C_6H_3(OMe)\cdot CH{:}CH\cdot CO\cdot C_{10}H_6\cdot OH,$$

prepared from vanillin, 2-aceto-1-naphthol, alcohol, and sodium hydroxide solution, crystallises from alcohol in red needles, m. p. 190—191°. Its solution in concentrated sulphuric acid has a reddish-yellow colour. The *diacetyl* derivative, $C_{24}H_{20}O_6$, crystallises in yellow needles, m. p. 162—164°.

The presence of the CO·C:C group in curcumin is proved by the fact that ferulic acid (4-hydroxy-3-methoxycinnamic acid) is formed when curcumin is boiled with 20% potassium hydroxide solution. The formula $[OH\cdot C_6H_3(OMe)\cdot CH{:}CH\cdot CO]_2CH_2$ is suggested as accounting for all the properties of curcumin. The formula $C_{21}H_{20}O_6$ (compare Latham and Loring Jackson, Abstr., 1908, i, 670) has been confirmed by conversion of curcumin into its *dicarbomethoxy*-derivative,

$$C_{19}H_{12}O_2(O\cdot CO_2Me)_2(OMe)_2,$$

deep yellow prisms, m. p. 150°, and its *dicarboethoxy*-derivative,

$$C_{19}H_{12}O_2(O\cdot CO_2Et)_2(OMe_4)_2,$$

yellow plates, m. p. 149—150°.

Hydroxylamine reacts with the dicarbethoxy-derivative, yielding 3 : 3′-*dimethoxy*-4 : 4′-*dicarbethoxy-αγ-distyryl*-*isooxazole*,

$$CH\ll \begin{matrix} C[CH{:}CH\cdot C_6H_3(OMe)(OH)]{:}N \\ C[CH{:}CH\cdot C_6H_3(OMe)(OH)]\cdot O \end{matrix}\gg CH,$$

as colourless plates, m. p. 139—140°. The same compound can also be obtained by the action of ethyl chloroformate on Ciamician and Silber's oxime-anhydride, $C_{21}H_{19}O_5N$ (Abstr., 1897, i, 229).

J. J. S.

C- and *O*-Acyl Derivatives of Coumaranones or 2-Hydroxycoumarones. Karl Auwers (*Ber.*, 1910, 43, 2192—2202).—By the interaction of organic bases and esters of 3-chloroacetyl-*p*-cresol, compounds of the type $C_6H_3Me(OH)\cdot CO\cdot CH_2\cdot NPh\cdot COR$ are formed, together with other substances containing nitrogen (compare Auwers, Abstr., 1909, i, 222). In presence of weak alkalis, the reaction takes quite another course, nitrogen-free substances being the sole product. These were at first taken to be flavonols or chromonols, but this idea was disproved by comparison with 2-methylflavonol, and the new compounds shown to be keto-derivatives of 4-methylcoumarone,

$$C_6H_3Me\ll \begin{matrix} C(OH) \\ O\text{——} \end{matrix}\gg C\cdot COR.$$

They form salts, ethers, and esters, and where $R = CH_3$ behave as ketones, although when R is an aromatic radicle, steric influences

prevent the formation of ketonic derivatives. Of the three possible desmotropic structural formulæ for the new compounds, the above is shown to be the most probable, and they are 1- or *C*-acyl-2-hydroxycoumarone derivatives, isomeric with the *O*-acyl compounds,

$$C_6H_4<\begin{matrix}C\cdot O\cdot COR\\ O\text{———}\end{matrix}>CH,$$

formed by acylation of coumaranones. The esters of the new ketones represent mixed *O,C*-diacyl derivatives. 3-Chloroacetyl-*p*-cresol forms an *anisoyl* derivative crystallising in short, lustrous, pointed prisms, m. p. 121·5°.

2-*Hydroxy*-1-*benzoyl*-4-*methylcoumarone*,

$$C_6H_3Me<\begin{matrix}C(OH)\\ O\text{———}\end{matrix}>C\cdot CO\cdot C_6H_5,$$

produced by boiling a mixture of 3-chloroacetyl-*p*-cresol, potassium carbonate and benzene, has m. p. 112°, and crystallises from alcohol in pale yellow, silky needles, which change readily into short, lustrous, four-sided plates. The compound forms a sparingly soluble *sodium* salt, dissolves in sodium hydroxide with an intense yellow coloration, and in sulphuric acid gives a yellow solution with a green fluorescence. It does not react with ketone reagents. The *acetate* crystallises in stellar aggregates of short, glistening needles, m. p. 81—82°. The *benzoate* forms colourless, glistening prisms, m. p. 137°.

2-*Hydroxy*-1-*anisoyl*-4-*methylcoumarone* forms long, slender, sulphur-yellow, lustrous needles, m. p. 145·5°.

2-*Hydroxy*-1-*acetyl*-4-*methylcoumarone*, $C_6H_3Me<\begin{matrix}C(OH)\\ O\text{———}\end{matrix}>C\cdot COMe$, crystallises in long, glistening needles, m. p. 86—87°; it is coloured orange-yellow by sulphuric acid. Alkaline hydrogen peroxide oxidises it to *p*-homosalicylic acid. The *benzoate* separates in colourless, matted needles, m. p. 128—129°; the *semicarbazone* forms colourless or slightly yellow needles, which become yellow at 195°, m. p. 202° (decomp.). The *phenylhydrazone* forms long, yellow needles, m. p. 128°.

2-*Benzoyloxy*-4-*methylcoumarone*, $C_6H_3Me<\begin{matrix}C(OBz)\\ O\text{———}\end{matrix}>CH$, prepared from methylcoumaranone, benzoyl chloride, and sodium hydroxide, forms yellow needles, m. p. 64—65°. E. F. A.

The Coumarone Group. A. von Graffenried and Stanislaus von Kostanecki (*Ber.*, 1910, **43**, 2155—2157. Compare Abstr., 1908, i, 442; 1909, i, 319).—Ethyl bromoacetate reacts with quinacetophenone monomethyl ether in the presence of sodium ethoxide, yielding *ethyl* 2-*acetyl*-4-*methoxyphenoxyacetate*, $OMe\cdot C_6H_3Ac\cdot O\cdot CH_2\cdot CO_2Et$, and this when hydrolysed with alcoholic potassium hydroxide yields the corresponding *acid*, $C_{11}H_{12}O_5$, which crystallises in broad needles, m. p. 144—145°. 4-*Methoxy*-2-*methylcoumarone*,

$$OMe\cdot C_6H_3<\begin{matrix}O\text{——}\\ CMe\end{matrix}>CH,$$

obtained by heating the acid with acetic anhydride and sodium acetate, is a colourless oil, b. p. 245°/706 mm., with an aromatic odour. Its

solution in concentrated sulphuric acid has an orange colour with a green fluorescence.

2-Acetyl-4-ethoxyphenoxyacetic acid, $OEt\cdot C_6H_3Ac\cdot O\cdot CH_2\cdot CO_2H$, crystallises in needles, m. p. 138—139°, and *4-ethoxy-2-methylcoumarone*, $C_{11}H_{12}O_2$, is a colourless oil, b. p. 257°/718 mm.

2-Acetyl-5 : 6-dimethoxyphenoxyacetic acid,

$$C_6H_2Ac(OMe)_2\cdot O\cdot CH_2\cdot CO_2H,$$

obtained from gallacetophenone methyl ether, has m. p. 104—106°, and *5 : 6-dimethoxy-2-methylcoumarone*, $C_6H_2(OMe)_2<\overset{O---}{CMe}>CH$, has b. p. 278—279°/702 mm. J. J. S.

Derivatives of 2-Styrylcoumarone. J. Abelin and Stanislaus von Kostanecki (*Ber.*, 1910, 43, 2157—2162. Compare preceding abstract).—*2-Cinnamoyl-5-methoxyphenoxyacetic acid*,

$$CHPh{:}CH\cdot CO\cdot C_6H_3(OMe)\cdot O\cdot CH_2\cdot CO_2H,$$

obtained by condensing benzaldehyde and 2-acetyl-5-methoxyphenoxyacetic acid (Abstr., 1909, i, 319) in the presence of alkali, crystallises from alcohol in colourless plates, m. p. 166—167°. The *ethyl* ester, $C_{20}H_{20}O_5$, forms colourless needles, m. p. 89°. *5-Methoxy-2-styrylcoumarone*, $OMe\cdot C_6H_3<\overset{O\cdot CH}{\underset{C\cdot CH{:}CHPh}{\|}}>$, is formed when the acid is heated with acetic anhydride and sodium acetate. It crystallises from alcohol in colourless needles, m. p. 77—78°, and gives a bright red colour when moistened with concentrated sulphuric acid.

5 : 2′-Dimethoxy-2-cinnamoylphenoxyacetic acid,

$$OMe\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot C_6H_3(OMe)\cdot O\cdot CH_2\cdot CO_2H,$$

obtained from *o*-methoxybenzaldehyde and 2-acetyl-5-methoxyphenoxyacetic acid, crystallises from alcohol in yellow prisms or colourless needles, m. p. 128°. The *ethyl* ester, $C_{21}H_{22}O_6$, has m. p. 111°, and *5 : 2′-dimethoxy-2-styrylcoumarone*, $C_{18}H_{16}O_3$, crystallises from alcohol in rhombic plates, m. p. 75°.

5 : 3′-Dimethoxy-2-cinnamoylphenoxyacetic acid, $C_{19}H_{18}O_6$, forms colourless needles, m. p. 142—143°; its *ethyl* ester, $C_{21}H_{22}O_6$, has m. p. 96°, and *5 : 3′-dimethoxy-2-styrylcoumarone*, $C_{18}H_{16}O_3$, crystallises in needles or plates, m. p. 120—121°.

5 : 4′-Dimethoxy-2-cinnamoylphenoxyacetic acid has m. p. 162—163°; its *ethyl* ester has m. p. 117°, and *5 : 4′-dimethoxy-2-styrylcoumarone* has m. p. 126°.

5 : 3′ : 4′-Trimethoxy-2-cinnamoylphenoxyacetic acid,

$$C_6H_3(OMe)_2\cdot CH{:}CH\cdot CO\cdot C_6H_3(OMe)\cdot O\cdot CH_2\cdot CO_2H,$$

obtained from veratraldehyde, crystallises in plates, m. p. 175°, and gives a dark red coloration with concentrated sulphuric acid. The *ethyl* ester, $C_{22}H_{24}O_7$, crystallises in yellow plates, m. p. 129—130°, and *5 : 3′ : 4′-trimethoxy-2-styrylcoumarone*, $C_{19}H_{18}O_4$, forms colourless needles, m. p. 106°. Its solution in sulphuric acid has a magenta-red colour. All attempts to transform this compound into a trimethoxydihydro*iso*brasan by ring formation proved fruitless. J. J. S.

Formation of Pyrene from Thebaine. Martin Freund (*Ber.* 1910, 43, 2128—2130).—The formation of pyrene from thebaine is

confirmed (compare Freund, Abstr., 1897, i, 496). Pyrene is formed, not merely when the alkaloid is distilled with zinc dust, but also when it is reduced with hydriodic acid and red phosphorus. The latter fact invalidates to a large extent Pschorr's criticism (this vol., i, 423) of the author's formula for thebaine. J. J. S.

New Preparation of 1-Alkylpyrrolidines. Karl Löffler (*Ber.*, 1910, **43**, 2035—2048. Compare Abstr., 1909, i, 830).—The method previously described, bromination of an amine at the nitrogen atom and elimination of hydrogen bromide by means of concentrated sulphuric acid, has been extended to the preparation of 1-methyl-2-propylpyrrolidine and of 1 : 2-dimethyl-, 1-methyl-2-ethyl-, and 1 : 3-dimethyl-pyrrolidines. Attempts were made to extend it to such amines as would yield piperidine derivatives or four-membered rings, but without result.

[With Curt Freytag.]—*δ-Methylamino*-n-*heptane*, prepared from methylamine and dipropyl ketone, and subsequent reduction, has b. p. 148°, D^{15} 0·77; the *aurichloride* separates in well formed yellow needles, m. p. 99°; the *platinichloride* forms orange plates, m. p. 193—195°; the *picrate* separates in long, light yellow needles, m. p. 96°; the *hydrochloride* is very hygroscopic.

1-*Methyl*-2-*propylpyrrolidine* is a colourless liquid, b. p. 146—147°/761 mm., D^{15} 0·815. The *picrate* forms yellow needles, m. p. 124°; the *platinichloride* forms orange plates, m. p. 145—146°; the *aurichloride* also forms yellow plates, m. p. 76°. The *ethochloride* gives a *platinichloride*, orange plates, m. p. 226—227°, and an easily decomposed yellow *aurichloride*.

Methyl-n-*amylamine* has b. p. 116—118°, D^{15}_{4} 0·738; the *picrate* forms yellow needles, m. p. 119—120°; the *hydrochloride* forms needles, m. p. 181—182°; the *platinichloride* separates in yellow needles, m. p. 171—173°; the *aurichloride* is a yellow oil. It could be converted into 1-methylpiperidine in the manner described.

β-Methylamino-n-*butane* has b. p. 78—79°, D^{15} 0·74; the *aurichloride* forms yellow needles, m. p. 58°; the *platinichloride* forms dark orange crystals, m. p. 151°; the *picrate* forms light yellow needles, m. p. 78°. No ring compound was formed on heating the brominated amine with concentrated sulphuric acid.

[With Marian Lukowsky.]—Methyl*iso*amylamine (compare Stoermer and Lepel, Abstr., 1896, i, 663) has b. p. 108—110°, D^{22}_{4} 0·7428; hydrochloride, m. p. 181°; platinichloride, m. p. 208—209°; aurichloride, needles, m. p. 68—70°; *picrate*, m. p. 112°.

1 : 3-*Dimethylpyrrolidine* has an odour of piperidine, b. p. 96—97°, D^{15}_{4} 0·792. The *picrate* shows dimorphism, separating first in long crystals, m. p. 181—182°, which change when kept in alcoholic solution into granular crystals, m. p. 110—115°: these on recrystallisation give the less fusible variety. The *hydrochloride* is hygroscopic; the *platinichloride* forms garnet-red, granular crystals, m. p. 58—59°; the *aurichloride* crystallises in characteristic, feathery, interlaced needles, m. p. 137°; the *mercurichloride* has m. p. 200—201°. The *ethiodide* is a hygroscopic, colourless powder; of the *ethochloride* the

platinichloride has m. p. 243—244° (decomp.); the *aurichloride*, m. p 200—201°.

[With Waldemar Bobiloff.]—*β-Methylamino-n-pentane*, from methylamine and methyl propyl ketone, is a colourless, mobile liquid, b. p. 103—104°/754 mm., D^{20} 0·747. The *platinichloride* forms yellowish-red needles, m. p. 137·5°; the *aurichloride* is an oil; the *picrate* forms broad needles, m. p. 77—78°. It is readily converted into 1 : 2-dimethylpyrrolidine, of which the *picrate* has m. p. 233·5°, and the *platinichloride* of the *ethochloride*, m. p. 249° (decomp.).

γ-Methylaminohexane is a transparent, mobile, strongly basic liquid, b. p. 126—128°/754 mm., D^{20} 0·761. The *platinichloride* is a flesh-coloured powder, m. p. 162—163°; aurichloride and picrate are oily.

1-*Methyl*-2-*ethylpyrrolidine* is a transparent, strongly basic liquid, b. p. 122—123°/762 mm., D^{15} 0·8124. The *platinichloride* forms intergrown needles, m. p. 210—211°; the *aurichloride*, well formed needles, m. p. 112°; the *picrate*, golden-yellow plates, m. p. 170°. The *platinichloride* of the *ethochloride* begins to decompose at 243°, m. p. about 250°. E. F. A.

Synthesis of δ-Methylconidine and of Derivatives of 2-Methyl-6-ethylolpiperidine. Karl Löffler and Hans Remmler (*Ber.*, 1910, **43**, 2048—2059. Compare Königs and Happe, Abstr., 1903, i, 850; Löffler and Thiel, Abstr., 1909, i, 182).—By the condensation of 2 : 6-lutidine with formaldehyde, 2-methyl-6-ethylolpyridine, b. p. 126—128°/16 mm., and 2 : 6-diethylolpyridine, b. p. 185—195°/16 mm., are obtained. The former, when reduced by means of sodium and alcohol, gives 2-*methyl*-6-*ethylolpiperidine*; the crude base has b. p. 226—232°, and is a mixture of stereoisomerides. One form separates from ether in glistening, rhombic crystals, m. p. 95—96°; the *aurichloride* has m. p. 104°; the *platinichloride* forms broad crystals, m. p. 180—181°; the *picrate* has m. p. 127°. The stereoisomeride was obtained as a viscid syrup, of which the *picrate* separates in long needles, m. p. 187°; the *aurichloride* has m. p. 99—100°; the *platinichloride* forms short, granular crystals, m. p. 198—199°.

2-Methyl-6-ethylolpiperidine has very little poisonous action. Attempts to resolve it into optically active modifications by means of tartaric acid were not successful.

When heated under pressure with fuming hydrochloric acid and red phosphorus, a *hydriodide iodide* is formed, crystallising in colourless, short needles, m. p. 192—193°. On warming with sodium hydroxide, this is converted into δ-*methylconidine*, $\begin{matrix}CH_2\cdot CH_2 & CH\cdot CH_2\\ | & | \\ CH_2\cdot CHMe\cdot N & CH_2\end{matrix}$, a colourless, mobile liquid with an unpleasant coniceine like odour, b. p. 156°, D_4^{15} 0·8931. The *picrate* forms large, pointed needles, m. p. 237°; the *aurichloride* is amorphous, m. p. 191—192°; the *platinichloride* forms broad needles, m. p. 198°. The *ethiodide* has m. p. 202° (decomp.); the *platinichloride* of the *ethochloride* has m. p. 210·5°.

By the action of phosphorus pentachloride on 2-methyl-6-ethylolpiperidine, 2-*methyl*-6-*vinylpiperidine* is obtained; the colourless, mobile liquid has b. p. 150°, D_4^{15} 0·8381. The *hydrochloride* forms colourless, slender needles, m. p. 242·5—243°; after crystallisation of

the salt, the mother liquors become an intense red colour after a time. The *picrate* crystallises in tabular plates, m. p. 123°; the *platinichloride* in long needles, m. p. 176°.

Chromic acid oxidises 2-methyl-6-ethylolpiperidine to 2-*methylpiperidyl*-6-*acetic acid*, crystallising in colourless, matted needles, m. p. 219—220°. The *hydrochloride* crystallises similarly, m. p. 192—206° (decomp.); the *aurichloride* forms needles, m. p. 129—131°; the *platinichloride*, granular crystals, m. p. 207°.

2 : 6-*Diethylolpiperidine* is obtained by reducing diethylolpyridine as a viscid oil, b. p. 168—169°/18 mm.; it crystallises in reniform aggregates. The *picrate* has m. p. 136°.

On acetylating 2-methyl-6-ethylolpiperidine with warm acetic anhydride, a *diacetate* is formed, a colourless, viscid liquid, b. p. 190—200°/25 mm., D_4^{15} 1·703; the two acetyl groups are probably attached to nitrogen and in the side-chain respectively; both are hydrolysed by 1% alcoholic hydrochloric acid. Acetylation in the cold with acetic anhydride gives the *monoacetate*, b. p. 105—110°/25 mm., a mobile, colourless, strongly alkaline liquid, which forms stable salts, and therefore is acetylated in the side-chain. The *aurichloride* crystallises in reniform aggregates, m. p. 118°. It was not found possible to cause this acetyl group to wander to the nitrogen atom. E. F. A.

Stereochemistry of Quinquevalent Nitrogen. Max Scholtz (*Ber.*, 1910, **43**, 2121—2126. Compare Abstr., 1904, i, 1044; 1905, i, 296, 473; 1908, i, 678; Scholtz and Wassermann, 1907, i, 340; Voss and Gadamer, this vol., i, 415).—Two stereoisomeric quaternary ammonium salts are formed by the union of allyl iodide with *dl*-6-phenyl-2-methyl-1-ethylpiperidine, and from these quaternary salts well defined, crystalline isomeric platinichlorides have been prepared.

Stereoisomeric quinquevalent nitrogen compounds of the type Na_2bcd have been prepared by condensing *o*-xylylene bromide with 2-phenyl-6-methylpiperidine (compare Abstr., 1898, i, 565). These compounds differ from the stereoisomerides described by Aschan (Abstr., 1904, i, 350), as they contain only one nitrogen atom.

6-*Phenyl*-2-*methyl*-1-*propylpiperidine*, $NPr<^{CHMe\cdot CH_2}_{CHPh\cdot CH_2}>CH_2$, prepared by boiling 2-phenyl-6-methylpiperidine (Scholtz and Müller, Abstr., 1901, i, 41) with *n*-propyl iodide and potassium hydroxide, is a colourless liquid with a basic odour, has b. p. 264—265° (corr.) and D_4^{20} 0·9101. It combines with benzyl iodide, yielding an oily 2-*phenylbenzyl*-6-*methyl*-n-*propylpiperidinium iodide*, $C_{22}H_{30}NI$, from which only a small amount of colourless crystals were isolated.

dl-2-*Phenyl*-6-*methyl*-1-*ethyl*-1-*allylpiperidinium iodide*,

$$C_3H_5\cdot NEtI<^{CHMe\cdot CH_2}_{CHPh\cdot CH_2}>CH_2,$$

exists in an oily (α) and a crystalline (β) form. The latter forms colourless prisms, m. p. 198°. The *α-platinichloride*, $(C_{17}H_{26}N)_2PtCl_6$, crystallises in orange-red needles, m. p. 211° (decomp.); the isomeric compound forms similar needles, m. p. 223°. The two *hydrochlorides* are deliquescent solids. The *α-aurichloride* is an oil which solidifies to

a resinous mass, and the *β-aurichloride*, $C_{17}H_{26}NAuCl_4$, crystallises in golden, yellow needles, m. p. 136°.

*α-2-l'henyl-*1-*o-xylylene-*6-*methylpiperidinium bromide*,

$$C_6H_4\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle NBr\langle\begin{matrix}CMe\text{-}CH_2\\CPh\text{-}CH_2\end{matrix}\rangle CH_2,$$

crystallises from water in rhombic prisms, m. p. 226°. The *β-compound* separates from solvents as an oil which solidifies when rubbed; it has m. p. 228°. The *α-platinichloride* has m. p. 238°, and the *β*-compound, m. p. 259°. The aurichlorides are oily. J. J. S.

An Acetato-Pyridine-Iron Base and a Very Basic Pyridine-containing Ferric Acetate. Rudolf Weinland and E. Gussmann (*Ber.*, 1910, **43**, 2144—2149).—By the action of pyridine on the acetate of the hexa-acetato-triferri-base (Abstr., 1909, i, 872), brownish-yellow salts have been obtained containing two atoms of iron and two molecules of pyridine in the cation.

$$\left[\begin{matrix}(OAc)_3\\Fe_2(C_5H_5N)_2\\OH\end{matrix}\right](OAc)_2$$

The *acetate* (annexed formula) is obtained by leaving 20 grams of the monoacetate of the hexa-acetato-triferri-base in contact with 50—60 grams of anhydrous pyridine at the ordinary temperature. The monoacetate dissolves, and then the acetate of the acetato-pyridine-iron base separates as a brownish-yellow powder, consisting of microscopic four-and six-sided plates.

$$\left[\begin{matrix}(OAc)_3\\Fe_2(C_5H_5N)_2\\OH\end{matrix}\right]OAc$$

The *iodide* (annexed formula) separates as a brownish-yellow precipitate when a saturated solution of potassium iodide is added to the freshly prepared solution of the acetate. The *thiocyanate*,

$$\left[\begin{matrix}(OAc)_3\\Fe_2(C_5H_5N)_2\\OH\end{matrix}\right](CNS)_2 + \left[\begin{matrix}(OAc)_3\\Fe_2(C_5H_5N)_2\\OH\end{matrix}\right]OAc\,CNS,$$

separates as a chocolate-brown powder on the addition of a saturated solution of sodium thiocyanate to the aqueous solution of the acetate. Under the same conditions, a saturated solution of potassium permanganate gives a rose-red precipitate of the permanganate,

$$\left[\begin{matrix}(OAc)_3\\Fe_2(C_5H_5N)_2\\(OH)_2\end{matrix}\right]MnO_4 + \left[\begin{matrix}(OAc)_3\\Fe_2(C_5H_5N)_2\\OH\end{matrix}\right](OAc)_2.$$

When 5 grams of pyridine are added to 30 c.c. of a 12% solution of the monoacetate of the hexa-acetato-triferri-base (*loc. cit.*) and the solution maintained at a temperature not exceeding 15°, dark red crystals of a pyridine-containing basic ferric acetate,

$$Fe_2O(OH)(OAc)_3{\cdot}C_5H_5N,$$

separate after some hours. A copper-red acetate of a pyridine-containing acetato-iron base has also been obtained, but requires further investigation. T. S. P.

Derivatives of Tetrahydroquinoline. III. Ketones and Acids of Tetrahydroquinoline and of Tetrahydro-*o*- and *p*-toluquinoline. Franz Kunckell (*Ber. Deut. pharm. Ges.*, 1910, 20, 277—293).—The interaction of 1-acetyltetrahydroquinoline, chloroacetyl chloride, and aluminium chloride in carbon disulphide leads to

the formation of 1-*acetyl*-6-*chloroacetyltetrahydroquinoline*,

$$CH_2Cl\cdot CO\cdot C_6H_3<\begin{matrix}CH_2-CH_2\\ |\quad\quad |\\ NAc\cdot CH_2\end{matrix}>,$$

m. p. 137°, which is converted into 1-*acetyltetrahydroquinoline*-6-*carboxylic acid*, m. p. 187°, by hot alkaline hydrogen peroxide, into a *trinitrotetrahydroquinoline*, m. p. 152°, by concentrated nitric acid, and into 1-*acetyl*-6-*chlorobromoacetyltetrahydroquinoline*, m. p. 179°, by bromination in glacial acetic acid; the last-mentioned compound is oxidised to the preceding acid, m. p. 187°, by alkaline hydrogen peroxide. The hydrolysis of 1-acetyl-6-chloroacetyltetrahydroquinoline by 20% hydrochloric acid on the water-bath yields 6-*chloroacetyltetrahydroquinoline*, m. p. 123—124°, an alcoholic solution of which at 5—10° is converted by nitrous fumes into the *nitrosoamine*, m. p. 140°.

1-*Acetyl*-6-*bromoacetyltetrahydroquinoline* has m. p. 134°.

1-Acetyl-6-methyltetrahydroquinoline is not only attacked more readily than 1-acetyltetrahydroquinoline by chloroacetyl chloride or bromoacetyl bromide, but reacts even with acetyl bromide itself, which is not the case with 1-acetyltetrahydroquinoline. 1-?-*Diacetyl*-6-*methyltetrahydroquinoline* has m. p. 160°. 1-*Acetyl*-?-*chloroacetyl*-6-*methyltetrahydroquinoline*, m. p. 132°, and 1-*acetyl*-?-*bromoacetyl*-6-*methyltetrahydroquinoline*, m. p. 128°, are obtained in the same manner as 1-acetyl-6-chloroacetyltetrahydroquinoline, and are converted into the following substances by reactions similiar to those mentioned above: 1-*acetyl*-6-*methyltetrahydroquinolinecarboxylic acid*, $CO_2H\cdot C_6H_2Me<\begin{matrix}CH_2-CH_2\\ |\quad\quad |\\ NAc\cdot CH_2\end{matrix}>$, m. p. 201°; *chloroacetyl*-6-*methyltetrahydroquinoline*, m. p. 122°, (*hydrochloride*, m. p. 218°); 1-*acetyl*-?-*chlorobromoacetyl*-6-*methyltetrahydroquinoline*, m. p. 143°; when heated with concentrated nitric acid, 1-acetyl-?-chloroacetyl-6-methyltetrahydroquinoline yields a *substance*, m. p. 259° (decomp.), which is probably a nitropiperidinecarboxylic acid.

The following derivatives of 1-acetyl-8-methyltetrahydroquinoline are obtained by similar processes: 1-*acetyl*-?-*chloroacetyl*-8-*methyltetrahydroquinoline*, m. p. 120°; 1-*acetyl*-?-*bromoacetyl*-8-*methyltetrahydroquinoline*, m. p. 125—126°; 1-*acetyl*-8-*methyltetrahydroquinolinecarboxylic acid*, m. p. 108°; the acetyl group cannot be introduced into 1-acetyl-8-methyltetrahydroquinoline. C. S.

Method of Preparation of α-Benzoylated Phenylhydrazines. Georg Lockemann (*Ber.*, 1910, **43**, 2223—2230).—Lockemann and Liesche (Abstr., 1905, i, 570) have shown that by the action of benzoyl chloride on phenylethylidenehydrazine in presence of dry pyridine, α-benzoyl-α-phenyl-β-ethylidenehydrazine is obtained. It is absolutely necessary to exclude all traces of moisture, otherwise the ethylidene group is eliminated, and di- and tri-benzoyl derivatives are obtained. Using dry pyridine, it is possible to benzoylate also with *m*- and *p*-nitro- and *p*-chloro-benzoyl chloride, but not with the *o*-nitro-derivative.

The action of excess of mineral acids in cold solution eliminates the ethylidene group from these hydrazines as aldehyde, and the salts of α-benzoylhydrazones are obtained.

[With Th. Lobenstein, H. Ende, and F. Herold.]—α-Benzoyl-α-phenyl-β-ethylidenehydrazine forms colourless, rectangular plates, m. p. 90—91°. It gives α-benzoylphenylhydrazine (Michaelis and Schmidt, Abstr., 1887, 820), m. p. 70°; the hydrochloride forms colourless needles, m. p. 202°.

α-p-*Nitrobenzoyl-α-phenyl-β-ethylidenehydrazine* crystallises in light yellow prisms with pointed ends, m. p. 116—117°; alcoholic hydrogen chloride converts it into the *hydrochloride* of α-p-*nitrobenzoyl-α-phenylhydrazine*, also crystallising in light yellow needles, which sinter at 183°, m. p. 195—196° (decomp.). The free base forms light yellow, lustrous crystals, m. p. 141—142°; the acetyl derivative, α-p-*nitrobenzoyl-β-acetyl-α-phenylhydrazine*, separates in light yellow crystals, m. p. 184—185°.

α-m-*Nitrobenzoyl-α-phenyl-β-ethylidenehydrazine* forms yellowish-white plates, m. p. 124—125°; α-m-*nitrobenzoylphenylhydrazine* forms yellowish-white, six-edged plates, m. p. 123—124°; the *hydrochloride* crystallises in yellowish-white, pointed needles, m. p. 176—177° (decomp.).

α-p-*Chlorobenzoyl-α-phenyl-β-ethylidenehydrazine* was obtained in yellow, short, rhombic crystals and in colourless, reniform prisms, both m. p. 90—91°. On keeping, the colourless prisms slowly change to the yellow, stable form; on crystallisation, the labile, colourless forms are the first to separate.

When moisture is present, p-*chlorobenzoic anhydride* is obtained, instead of the foregoing; it crystallises in lustrous, long, colourless prisms and needles, m. p. 193—194°.

α-p-*Chlorobenzoyl-α-phenylhydrazine* forms colourless rhombs with pointed angles, m. p. 128—129°. The *hydrochloride* crystallises in colourless, lustrous needles, m. p. 192—193°. E. F. A.

Syntheses of Polypeptides. Derivatives of Pyrrolidonecarboxylic Acid. Emil Abderhalden and Akikazu Suwa (*Ber.*, 1910, **43**, 2151—2155).—*Pyrrolidonecarboxylic chloride* can be obtained by the action of thionyl chloride or of a mixture of acetyl chloride and phosphorus pentachloride on the acid, and condenses with ethyl glycine, yielding *ethyl pyrrolidonylglycine*, $C_9H_{14}O_4N_2$, which crystallises from alcohol in colourless needles, m. p. 134° (corr.). When hydrolysed with concentrated hydrochloric acid, the ester yields the hydrochlorides of glutamic acid and of glycine ester.

Pyrrolidonylglycine, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CO—NH\end{matrix}\!\!>\!CH\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, can be prepared by hydrolysing the ester by shaking with *N*-sodium hydroxide solution; it crystallises in slender needles, m. p. 168° (corr.), and yields a hygroscopic *copper* salt, $(C_7H_9O_4N_2)_2Cu,2H_2O$. J. J. S.

Quinone Di-imines of the Acridone Series. Ludwig Kalb (*Ber.*, 1910, **43**, 2209—2214).—By the oxidation of the yellow quinacridone discovered by Ullmann and Maag (Abstr., 1906, i, 459) with lead oxide in indifferent solvents in presence of acetic acid, a new quinonedi-imine, *dehydroquinacridone*,

$$C_6H_4\!<\!\begin{matrix}CO\\ -N\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}N-\\ CO\end{matrix}\!>\!C_6H_4,$$

is obtained, which has a remarkable greenish dark-blue colour in solution.

It may be regarded as derived from quinonedianil,

$$C_6H_5\cdot N{:}C_6H_4{:}N\cdot C_6H_5,$$

which is orange-red; the colour is deepened to blue by the presence of the two acridone rings. The corresponding compound with but one acridone ring, *dehydro-2-anilinoacridone*, $C_6H_4\langle^{CO}_{N}\rangle C_6H_3{:}N\cdot C_6H_5$, obtained by the oxidation of 2-anilinoacridone with lead oxide, is dark red.

Dehydroquinacridone, like dehydroindigotin, has a strong oxidising action, and liberates other quinones and quinonedi-imines from their hydro-compounds, and oxidises indigotin to dehydroindigotin. The oxidising power may be determined by titration with ethereal quinol solution, the colour changing from blue through green to yellow. It liberates chlorine from cold fuming hydrochloric acid.

2-Anilinodehydroacridone does not possess such marked oxidising powers, but oxidises quinol to quinone.

Dehydroquinacridone crystallises in bluish-black, hexagonal plates. It dissolves in sulphuric acid with decomposition, showing a brownish-yellow coloration and green fluorescence.

4′-Anilinodiphenylamine-2-carboxylic acid,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NHPh,$$

prepared by the condensation of *p*-aminodiphenylamine with *o*-chlorobenzoic acid, crystallises in pale yellow plates, m. p. 199° (green coloration and decomp.). The colourless solution in sulphuric acid gives a cherry-red coloration with traces of nitric acid.

2-Anilinoacridone, prepared by warming the above compound with sulphuric acid at 85°, forms yellow, crystalline crusts, m. p. 303—305°. The solutions are yellow and fluoresce green; that in sulphuric acid is faintly red, and has an intense blue fluorescence. The *hydrochloride* forms long, red, prismatic plates, which change to yellow at 250°.

2-Anilinodehydroacridone forms long, pointed, blackish-brown plates, which partly melt at 145°, decomp. 280°. It dissolves and decomposes in sulphuric acid with a reddish-brown colour and blue fluorescence.

E. F. A.

Derivatives of Iminazole [Glyoxaline] and Histidine containing Iodine. Hermann Pauly (*Ber.*, 1910, **43**, 2243—2261. Compare Pauly and Gundermann, Abstr., 1909, i, 71).—It has been shown for triiodoglyoxaline that all three carbon atoms in the ring can fix iodine, and the preparation of a hydrochloride showed that no iodine was attached to nitrogen. This constitution is now confirmed by the preparation of a *silver* compound and of an *N-ethyl* derivative, and, further, by the continued action of iodine and alkali, leading to the formation of 1 : 2 : 4 : 5-*tetraiodoglyoxaline*, $\begin{matrix}CI\cdot NI\\ \|\ \ \rangle\\ CI{-}N\end{matrix}$CI. In addition, 4 : 5-*di-iodo-2-methylglyoxaline*, from 2-methylglyoxaline, 1 : 4 : 5-*tri-iodo-2-methylglyoxaline*, and 1-*iodo*-2 : 4 : 5-*trimethylglyoxaline*, $\begin{matrix}CMe\cdot NI\\ \|\ \ \rangle\\ CMe{-}N\end{matrix}$CMe, have

been prepared so as to allow of a comparison between glyoxalines containing iodine attached to C or N.

The C-compounds are more soluble, more definitely crystalline, they form metallic and acid salts, and melt without much loss of iodine.

The N-compounds are sparingly soluble in indifferent solvents, form a fine powder without crystalline structure, give no salts, and explode on heating, giving iodine vapour and leaving a black residue.

2:4:5-Tri-iodo-1-ethylglyoxaline, when boiled with sodium hydroxide, develops a strong odour of ethylcarbylamine.

Tetraiodoglyoxaline when heated decomposes at 160° into iodine and a black residue, which contains all the nitrogen, and about 25% of the iodine of the original substances. This iodine is not removed until the residue is heated to 400°, when it has the composition C_3N_2. At a temperature near a red heat, above 500°, this in turn decomposes to carbon and nitrogen. This behaviour is similar to that of cyanuric iodide, $C_3N_3I_3$, studied by Klason (Abstr., 1886, 1001).

Three derivatives of histidine, namely, benzoyl- and *p*-nitrobenzoyl-histidine and *l*-histidine anhydride, have been iodised; in each case two iodine atoms become attached to carbon in the glyoxaline nucleus, and the compounds are regarded as derivatives of the unknown di-iodo-histidine, $CI\langle\begin{matrix}N=CI\\ NH\cdot C\cdot CH_2\cdot CH(NH_2)\cdot CO_2H\end{matrix}$.

Preparation of the *disilver* salt in the case of *tetraiodohistidine anhydride* proved the nitrogen groups to have no iodine attached to them.

Iodine is the more easily introduced into glyoxalines the more basic they are; thus, 5-methylglyoxaline decolorises nearly 7/10 mol. iodine, glyoxaline only about 1/7 mol. Histidine and histidine anhydride behave much as glyoxaline, but the introduction of acyl residues, causing the bases to react acid towards litmus, almost destroys the power of taking up iodine.

The amount of iodine absorbed by sturine corresponds almost exactly with that required by the histidine contained in sturine.

Tri-iodoglyoxaline in small doses causes a marked quickening of the breathing and of the pulse.

2 : 4 : 5-*Tri-iodo*-1-*ethylglyoxaline* forms colourless crystals, m. p. 141—142°.

1 : 2 : 4 : 5-*Tetraiodoglyoxaline* is a colourless or yellowish-grey, odourless powder, decomp. 160°.

4 : 5-*Di-iodo*-2-*methylglyoxaline* crystallises in centimetre-long, thin, lustrous prisms, m. p. 199°; it dissolves in acids or alkalis, forming salts.

1 : 4 : 5-*Tri-iodo*-2-*methylglyoxaline* is a greyish-yellow, insoluble powder, decomp. 160°.

1-*Iodo*-2 : 4 : 5-*trimethylglyoxaline* is a cream-coloured, dust-like powder, m. p. 134° (decomp. and blackening).

Benzoylhistidine has m. p. 249° (Fränkel: 230°).

Benzoyldi-iodohistidine is a colourless, chalk-like powder, m. p. 161—164° in an evacuated tube.

p-Nitrobenzoyldi-iodohistidine has m. p. 172° (decomp.). Like the

foregoing, it gives an orange-red coloration with diazobenzenesulphonic acid and sodium carbonate, and forms a *silver* salt.

Tetraiodohistidine anhydride crystallises from alcohol in aggregates of minute, rectangular plates, m. p. 240° (in an evacuated tube) to a dark liquid.

The compound is amphoteric, and dissolves in both acids and alkalis; it reacts with diazobenzenesulphonic acid, dissolves in cold, strong acids without decomposition, and on heating with sulphuric acid gives iodine vapour at 150°. The *disilver* salt is at first colloidal, but subsequently flocculent; it explodes on heating.

Reduction by means of sulphites converts tetraiodohistidine anhydride into the *di-iodo*-compound; this forms a microcrystalline powder, m. p. 245° (decomp.).

Iodine is without action on alanine anhydride. E. F. A.

Carboxylic Derivatives of 3-Methyl- and 3-Phenyl-5-chloropyrazole. August Michaelis and Omar Schmidt (*Ber.*, 1910, **43**, 2116—2120).—Only a few pyrazole compounds containing acid groups attached to N have been prepared previously (compare Thiele and Heuser, Abstr., 1896, i, 340). Such compounds can be obtained by condensing the sodium derivatives of 5-chloro-3-methyl- and 5-chloro-3-phenyl-pyrazole with the esters of halogenated fatty acids.

5-Chloro-3-methylpyrazole-1-propionic acid,

$$\begin{matrix}\mathrm{CMe{=}N}\\ |\\ \mathrm{CH{\cdot}CCl}\end{matrix}\!\!>\!\mathrm{N{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H},$$

prepared by heating 5-chloro-3-methylpyrazole and ethyl β-iodopropionate with alcoholic sodium ethoxide on the water-bath for several hours, forms compact crystals, m. p. 94°. When heated above its m. p., the acid yields 5-chloro-3-methylpyrazole and acrylic acid.

The *ammonium* salt crystallises with 1EtOH; the *sodium* salt,

$$\mathrm{C_6H_8N_2Cl{\cdot}CO_2Na},$$

forms small needles; the *barium* salt, $(\mathrm{C_6H_8N_2Cl{\cdot}CO_2)_2Ba,3H_2O}$, crystallises in colourless plates; the *silver* salt forms a curdy precipitate; the *ethyl* ester, $\mathrm{C_6H_8N_2Cl{\cdot}CO_2Et}$, forms a pale yellow oil; the *methiodide*, $\mathrm{C_6H_8N_2Cl{\cdot}CO_2H,MeI}$, forms colourless prisms, m. p. 142°, and the *methiodide* of the ester has m. p. 136°.

5-Chloro-4-bromo-3-methylpyrazole-1-propionic acid,

$$\begin{matrix}\mathrm{CMe{=}N}\\ |\\ \mathrm{CBr{\cdot}CCl}\end{matrix}\!\!>\!\mathrm{N{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H},$$

obtained by brominating the previous acid in glacial acetic acid, forms compact crystals, m. p. 113°.

5-Chloro-3-methylpyrazole-1-acetic acid crystallises in colourless needles, m. p. 199°; the *ammonium* salt crystallises with 1EtOH; the *sodium* with $2{\cdot}5\mathrm{H_2O}$, and the *barium* with $5\mathrm{H_2O}$. The *ethyl* ester is a pale yellow oil; the *methiodide* has m. p. 156°, and the *methiodide* of the ethyl ester, m. p. 130°. *5-Chloro-4-bromo-3-methylpyrazole-1-acetic acid*, $\mathrm{C_5H_5N_2ClBr{\cdot}CO_2H}$, crystallises in nacreous plates, m. p. 197°.

Ethyl 5-chloro-3-methylpyrazole-1-carboxylate,

$$\mathrm{N}\!\!<\!\!\begin{matrix}\mathrm{N(CO_2Et)}\\ \mathrm{CMe{-}CH}\end{matrix}\!\!>\!\mathrm{CCl},$$

is a colourless oil, b. p. 127°/18 mm.; the free acid cannot be isolated, as it decomposes immediately into 5-chloro-3-methylpyrazole and carbon dioxide.

5-Chloro-3-phenylpyrazole-1-acetic acid, $C_{10}H_8N_2Cl\cdot CO_2H$, forms colourless needles, m. p. 166°. The *sodium* salt crystallises with $4{\cdot}5H_2O$, and the *barium* salt with $7H_2O$. Its 4-*bromo*-derivative, $C_{10}H_7N_2ClBr\cdot CO_2H$, forms colourless needles, m. p. 169°.

J. J. S.

Pyrines of 1 : 3-Dimethylpyrazolone. August Michaelis and August Lachwitz (*Ber.*, 1910, **43**, 2106—2115).—*5-Chloro-3-methylpyrazole*, $N\begin{matrix}NH-CCl\\ \| \\ CMe\cdot CH\end{matrix}$, prepared by the action of phosphoryl chloride on 3-methylpyrazolone at 150°, forms needles or rhombic crystals, m. p. 116°, b. p. 258°, and when heated at 140° for six hours with phosphorus pentachloride, yields 4 : 5-*dichloro-3-methylpyrazole*,

$$N\begin{matrix}NH-CCl\\ \| \\ CMe\cdot CCl\end{matrix}$$

which crystallises in felted needles, m. p. 128°, and is insoluble in acids. *5-Chloro-4-bromo-3-methylpyrazole*, $C_4H_4N_2ClBr$, obtained by the action of bromine on a glacial acetic acid solution of the 5-chloro-derivative, crystallises in glistening needles, m. p. 140°, and yields a *perbromide*, $C_4H_4N_2ClBr_3$, m. p. 186°. *5-Chloro-4-iodo-3-methylpyrazolone*,

$$C_4H_4N_2ClI,$$

also forms glistening needles, m. p. 152°. *5-Chloro-1-benzenesulphonyl-3-methylpyrazolone*, $N\begin{matrix}N(SO_2Ph)\\ | \\ CMe-CH\end{matrix}\!\!>\!CCl$, forms colourless crystals, m. p. 67°, and with bromine yields the 4-*bromo*-derivative, m. p. 117°.

5-Chloro-1 : 3-dimethylpyrazole methiodide, $NMeI\begin{matrix}NMe\cdot CCl\\ | \\ CMe-CH\end{matrix}$, prepared by heating 5-chloro-3-methylpyrazole with methyl iodide and alcohol at 100°, crystallises in colourless needles, m. p. 240°. The *methobromide* has m. p. 276°, and the *methochloride* contains $3H_2O$ and has m. p. 230°, or 252° anhydrous; the *platinichloride*,

$$(C_6H_{10}N_2Cl)_2PtCl_6,H_2O,$$

forms red, compact crystals, m. p. 243°; the *mercurichloride*,

$$C_6H_{10}N_2Cl_2,HgCl_2,$$

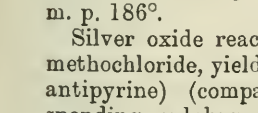
colourless plates, m. p. 136°, and the *picrate*,

$$C_6H_{10}N_2Cl,C_6H_3O_7N_3,$$

pale yellow needles, m. p. 132°.

5-Chloro-3-methyl-1-ethylpyrazole ethiodide forms colourless plates, m. p. 186°.

Silver oxide reacts with an aqueous solution of the methiodide, or methochloride, yielding 2 : 5-oxido-1 : 2 : 3-trimethylpyrazole (1-methylantipyrine) (compare Knorr, Abstr., 1906, i, 893). The corresponding sulphur compound, 2 : 5-*sulphido*-1 : 2 : 3-*trimethylpyrazole*,



obtained by the action of sodium sulphide on the methiodide or methochloride, contains $1{\cdot}5H_2O$, which it loses at 100—105°; when anhydrous it has m. p. 147°, and hydrated, m. p. 83°.

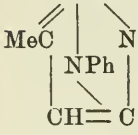
The *hydrochloride*, $C_6H_{10}N_2S,HCl$, forms large prisms, which deliquesce in the air; the *platinichloride*, $(C_6H_{10}N_2S)_2H_2PtCl_6$, forms a reddish-brown, amorphous powder, which decomposes at 320°; the *hydriodide* forms slender needles, m. p. 168°.

4-*Bromo*-2 : 5-*sulphido*-1 : 2 : 3-*trimethylpyrazole*, $C_6H_9N_2BrS$, prepared from the methiodide of 5-chloro-4-bromo-3-methylpyrazole, crystallises in colourless needles, m. p. 221°. The *trioxide*,

$$C_6H_{10}O_3N_2S,$$

can be prepared by passing chlorine into an aqueous solution of sulphido-1 : 2 : 3-trimethylpyrazole, or by the action of sodium sulphite on the methiodide of 5-chloro-1 : 3-dimethylpyrazole, and crystallises in colourless needles, m. p. 227° (decomp.). The thiopyrine combines with methyl iodide at the ordinary temperature, yielding the *methiodide*, $NMeI<\begin{matrix}NMe\\CMe\cdot CH\end{matrix}>C\cdot SMe$, as pale yellow, compact crystals, m. p. 199°; the corresponding *methochloride* contains $2H_2O$, and has m. p. 130°; the *platinichloride* forms golden-yellow needles, m. p. 225°. When the thiopyrine or its methiodide is distilled, the ψ-compound, 5-*methylthiol*-1 : 3-*dimethylpyrazole*, $N<\begin{matrix}NMe\\CMe-CH\end{matrix}>C\cdot SMe$, is obtained as a colourless oil, b. p. 243°; its *platinichloride* crystallises in golden-yellow plates, m. p. 264°, and its *nitroso*-derivative, $N<\begin{matrix}NMe\cdot C\cdot SMe\\CMe\cdot C\cdot NO\end{matrix}$, forms dark green, glistening needles. When oxidised with permanganate in acetic acid solution, the ψ-compound yields a *sulphone*, $C_6H_{10}O_2N_2S$, as colourless, glistening needles, m. p. 121°.

2 : 5-*Anilo*-1 : 2 : 3-*trimethylpyrazole* (1-*methylanilopyrine*), annexed formula, obtained by heating the methiodide or methochloride of chlorodimethylpyrazole with aniline at 124° for two hours, forms compact crystals, m. p. 82°; it is strongly alkaline, and rapidly absorbs carbon dioxide. The *hydrochloride*, $C_{12}H_{16}N_3Cl,2H_2O$, forms compact, colourless needles, m. p. 238° when anhydrous; the *platinichloride* forms golden-yellow needles, m. p. 207°; the *picrate*, $C_{12}H_{16}N_3,C_6H_3O_7N_3$, yellow prisms, m. p. 129°; the *chromate*, $(C_{12}H_{15}N_3)_2,H_2Cr_2O_7$, orange-yellow plates, m. p. 171°, and the *carbonate*, $C_{12}H_{15}N_3,H_2CO_3$, a colourless powder, m. p. 102° (decomp.). The *methiodide*, $NMeI<\begin{matrix}NMe\\CMe\cdot CH\end{matrix}>C\cdot NMePh$, forms slender, colourless needles, m. p. 200°, and the *propiodide*,

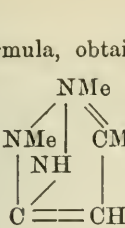


$$C_{12}H_{15}N_3,C_3H_7I,$$

compact crystals, m. p. 176°. When the methiodide is distilled under reduced pressure it yields the ψ-compound, 5-*methylanilino*-1 : 3-*dimethylpyrazole*, $N<\begin{matrix}NMe\\CMe\cdot CH\end{matrix}>C\cdot NMePh$, as a viscid, colourless oil, b. p. 165°/30 mm. Its *nitroso*-derivative, $C_{12}H_{14}ON_4$, forms dark green, compact crystals, m. p. 135°. When the hydrochloride is distilled under 30 mm. pressure, it yields methyl chloride and 5-*anilino*-1 : 3-*dimethylpyrazole*, $N<\begin{matrix}NMe\\CMe\cdot CH\end{matrix}>C\cdot NHPh$, m. p. 95°.

2 : 5-*Imino*-1 : 2 : 3-*trimethylpyrazole* (1-*methyliminopyrine*), annexed

formula, obtained by heating 5-chlorodimethylpyrazole methochloride



with aqueous ammonium hydroxide at 130°, forms a yellow oil, and yields a *hydrochloride* in the form of slender needles, m. p. 258°. The *aurichloride*, $C_6H_{11}N_3,HAuCl_4$, forms golden-yellow plates, m. p. 184°; the *platinichloride*, yellow needles, m. p. 210°. The base absorbs carbon dioxide rapidly. J. J. S.

1 : 2-Dimethoxyphenanthraphenazine. Ilie J. Pisovschi (*Ber.*, 1910, **43**, 2137—2144).—1 : 2-Dimethoxyphenanthraphenazine,

$$C_6H_2(OMe)_2\begin{matrix}N{:}C\cdot C_6H_4\\ \diagup\\ N{:}C\cdot C_6H_4\end{matrix}\diagdown,$$

has been synthesised from acetylvanillin by the following series of reactions: $CHO\cdot C_6H_3(OMe)\cdot OAc \longrightarrow CHO\cdot C_6H_2(OMe)(NO_2)\cdot OAc \longrightarrow CHO\cdot C_6H_2(OMe)(NO_2)\cdot OH \longrightarrow CHO\cdot C_6H_2(OMe)_2\cdot NO_2 \longrightarrow CO_2H\cdot C_6H_2(OMe)_2\cdot NO_2 \longrightarrow NH_2\cdot CO\cdot C_6H_2(OMe)_2\cdot NO_2 \longrightarrow NH_2\cdot C_6H_2(OMe_2)_2\cdot NO_2 \longrightarrow C_6H_2(\overset{1:2}{NH_2})_2(\overset{3:4}{OMe})_2 \longrightarrow C_6H_2(OMe)_2\begin{matrix}N{:}C\cdot C_6H_4\\ \diagup\\ N{:}C\cdot C_6H_4\end{matrix}\diagdown.$

A modification of Pschorr and Sumuleanu's method for the preparation of acetylvanillin (Abstr., 1900, i, 178) is described. *adj-o*-Nitroveratraldehyde is best prepared by methylating *o*-nitrovanillin with methyl sulphate and alkali; it has m. p. 63°, and when oxidised in acetone solution with aqueous permanganate yields *o*-nitroveratric acid, m. p. 203°.

The *chloride*, $NO_2\cdot C_6H_2(OMe)_2\cdot COCl$ [2 : 3 : 4 : 1], forms slender, colourless needles, m. p. 73°, and the *amide*, $NO_2\cdot C_6H_2(OMe)_2\cdot CO\cdot NH_2$, crystallises from toluene in long, colourless needles, m. p. 172°, and is resistent towards hydrolysing agents.

(adj)-3-*Nitro*-4-*aminoveratrole*, $NO_2\cdot C_6H_2(OMe)_2\cdot NH_2$, crystallises in red needles, m. p. 74°, and exhibits dichroism. When reduced with iron and acetic acid, it yields adj-*veratrylenediamine*, $C_6H_2(NH_2)_2(OMe)_2$, in silver-white plates, m. p. 97°. This base is much more stable than Moureu's *s*-veratrylenediamine (Abstr., 1897, i, 411). The halide salts form colourless needles, but their aqueous solutions have a cherry-red or reddish-violet colour. The base condenses with phenanthraquinone in the presence of acetic acid, yielding 1 : 2-*dimethoxyphenanthraphenazine* in yellow, felted needles, m. p. 174—175°. Its dilute solutions have a green fluorescence. The *hydrochloride* and *hydrobromide* are red; the *hydriodide*, brownish-black, and all three are hydrolysed by water. J. J. S.

Products of the Action of the Primary Amines on the Dinitrosacyls [Glyoximeperoxides]. II. Jacob Böeseken (*Rec. trav. chim.*, 1910, [ii], **14**, 275—292. Compare Abstr., 1898, i, 696).—Wieland and Semper have shown (Abstr., 1904, i, 54; 1908, i, 108) that the dinitrosacyls probably have the endoxyfurazan or furoxan, $\cdot C\begin{matrix}\diagup\\ \\ \diagdown\end{matrix}\overset{\|}{C}\cdot\\ \underset{\|}{N}\cdot O\cdot\underset{|}{N}\diagup O$, rather than the glyoxime-peroxide configuration, $\begin{matrix}\cdot C{:}N\cdot O\\ |\\ \cdot C{:}N\cdot O\cdot\end{matrix}$

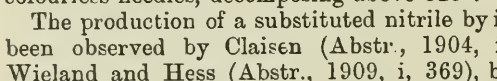
The conclusions drawn previously (Abstr., 1898, i, 696) from the

reactions of these compounds are now reconsidered in the light of Wieland and Semper's work.

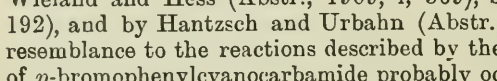
[With H. Couvert.]—Diphenyldinitrosacyl, prepared by Holleman's method (Abstr., 1893, i, 205), when heated in ethereal solution with *p*-bromoaniline (2 mols.) gives dark brown needles, decomposing at 126°, of *benzoyl*-p-*bromoanilinofurazan*, probably according to the following scheme:

If this furazan is heated on a water-bath with glacial acetic acid, it is transformed into an isomeride, which crystallises in colourless, felted needles, m. p. 208°. This isomeride is not attacked by concentrated sulphuric acid or by nitric acid (D 1·35), and, therefore, the presence of the ·CN group is very improbable, but it dissolves in potassium ethoxide solution, giving a golden-yellow liquid, which, on heating on a water-bath, becomes colourless, and yields the *potassium* salt of p-*bromophenylcyanocarbamide*. The free p-*bromophenylcyanocarbamide* forms colourless needles, decomposing above 325°.

The production of a substituted nitrile by intramolecular change has been observed by Claisen (Abstr., 1904, i, 14; 1909, i, 185), by Wieland and Hess (Abstr., 1909, i, 369), by Wolff (Abstr., 1895, i, 192), and by Hantzsch and Urbahn (Abstr., 1895, i, 393). From its resemblance to the reactions described by these authors, the formation of *p*-bromophenylcyanocarbamide probably occurs thus:

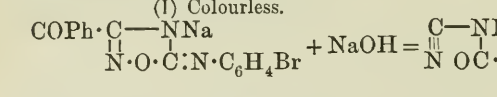


(I) Colourless. Golden-yellow.



Colourless.

The author considers that the colourless isomeride obtained from benzoyl-*p*-bromoanilinofurazan has the constitution of *benzoyl*-p-*bromoanilino-aβ'-furodiazole* (I), and is formed from the furazan by a partial Beckmann change, thus:



p-Bromophenylcyanocarbamide cannot be recrystallised from water owing to partial decomposition. It is decomposed by dilute hydrochloric acid according to the equation: $C_8H_6ON_3Br + 2H_2O = C_6H_4Br\cdot NH_2 + CO_2 + CO(NH_2)_2$. From conductivity measurements, the value $2\cdot4 \times 10^{-4}$ was obtained for its dissociation constant (K), whilst a colorimetric comparison (using Congo-red) with hydrochloric acid of different strengths gave $1\cdot8 \times 10^{-4}$.

A solution of the potassium salt of *p*-bromophenylcyanocarbamide gives a white, flocculent precipitate with silver nitrate, stable in the light and soluble in ammonia. The ammoniacal solution deposits small, brilliant crystals of the *silver ammonia* derivative, $C_8H_5ON_3BrAg,NH_3$, which are not acted on by light, but lose ammonia when heated.

Addition of a solution of copper sulphate to a solution of potassium *p*-bromophenylcyanocarbamide gives a yellowish-green, crystalline precipitate of the *copper* salt. The latter is a very sensitive reaction for all cyanocarbamides.

When the potassium salt is warmed at 50° with sulphuric acid or hydrogen peroxide (1·5 mols.) and a little potassium hydroxide solution (compare Radziszewski, Abstr., 1885, 496; Peski, Abstr., 1909, i, 647), *p-bromophenylbiuret*, $C_6H_4Br{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, is formed, which crystallises in long needles decomposing at 230° (approx.).

Similarly, when heated in a sealed tube at 100° with ammonium sulphide, the potassium salt is converted into *p-bromophenylthiobiuret*, $C_6H_4Br{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, which crystallises in long, silky needles, soluble in strong alkalis, from which it is precipitated by carbon dioxide. This thiobiuret has an extremely bitter taste, and loses sulphur when treated with ammoniacal silver or copper solutions.

E. H.

Aminophenazines. Alfred Wohl and Martin Lange (*Ber.*, 1910, **43**, 2186—2188).—2-Aminophenazine,

$$C_6H_4\begin{cases}N{\cdot}C{\cdot}CH{:}CH\\ \|\quad\quad|\\ N{\cdot}C{\cdot}CH{:}C{\cdot}NH_2\end{cases},$$

is formed when a mixture of *o*-nitroaniline, aniline hydrochloride, and finely-powdered zinc chloride is heated at 180—185° for half an hour. The same product is formed when formanilide is used in place of aniline hydrochloride. The m. p. of the pure product is 288° (corr.), not 274°.

Aminonaphthaphenazine, obtained by heating *o*-nitroaniline, α-naphthylamine, and zinc chloride at 150—180°, crystallises from xylene in yellowish-brown, glistening prisms, m. p. 294° (decomp.).

When substituted anilines are used instead of aniline or α-naphthylamine, the yields of phenazines are small. J. J. S.

Triazole and Tetrazole from Azoimide. Otto Dimroth and Gustav Fester (*Ber.*, 1910, **43**, 2219—2223).—Azoimide reacts with acetylene when heated in acetone solution for seventy hours at 100° in sealed tubes, forming 1 : 2 : 3-triazole, $NH\begin{cases}CH{:}CH\\ |\quad|\\ N{=}N\end{cases}$. This was identified by methylation of the silver salt to 1-*methyl*-1 : 2 : 3-*triazole*, which forms a very characteristic *aurichloride*, m. p. 160°.

Similarly, azoimide combines with hydrogen cyanide when heated for two to three days at 100° in alcoholic solution to form tetrazole, and this affords the best method of preparing tetrazole.

Phenylazoimide combines with acetylene when heated in acetone solution for forty hours to 1-phenyl-1 : 2 : 3-triazole. Phenylazoimide, however, does not condense with hydrogen cyanide or cyanogen, or with ethyl cinnamate. E. F. A.

The Oxidation of Some Azo-derivatives to the Corresponding Azoxy-compounds. Angelo Angeli (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 793—795).—Only a few instances of the oxidation of azo- to

azoxy-compounds are described in the literature, and some of these are doubtful.

If hydrogen peroxide is added to a solution of azobenzene in acetic acid, pure azoxybenzene is obtained in a few days. The reaction closely resembles the conversion of tertiary amines into their oxides by the same reagent. This result, taken together with other reactions studied by the author, favours the constitution $\begin{matrix} R\cdot N \\ \| \\ O \end{matrix} \!\!:\!\! \begin{matrix} N\cdot R \\ | \\ \end{matrix}$ for the azoxy-compounds. C. H. D.

Researches on Benzidine Formation. Henri Duval (*Bull. Soc. chim.* 1910, [iv], 7, 727—732. Compare this vol., i, 559, 588).—*2 : 2′-Hydrazodiphenylethane*, $C_6H_4<\begin{matrix}NH\text{–}NH \\ CH_2\cdot CH_2\end{matrix}>C_6H_4$, prepared by reducing 2 : 2′-azodiphenylethane (Abstr., 1909, i, 747) with zinc dust and barium hydroxide in aqueous alcoholic solution, forms yellowish-white crystals, m. p. 151°, which give only very small quantities of a colourless, nitrogenous, weakly basic, crystalline substance, m. p. 230°, when treated with hydrochloric acid. Like the corresponding methane derivative, 2 : 2′-azodiphenylethane, when reduced with a boiling hydrochloric acid solution of stannous chloride, gives 2 : 2′-diaminodiphenylethane, described by Busch and Weiss (Abstr., 1900, i, 699). The conclusion is drawn that the reactions in the diphenyl, diphenylmethane, and diphenylethane series are essentially different from those in the benzene series, since in the former cases the benzidine transformation does not occur. E. H.

Changes in the Physical Conditions of Colloids. X. Action of Organic Bases and Amphoteric Electrolytes on Albumin. Hans Handovsky (*Biochem. Zeitsch.*, 1910, **25**, 510—538. Compare this vol., i, 344).—The influence of bases and amphoteric electrolytes on the formation of albumin salts has been investigated by means of viscosity measurements. The comparative data indicate that the hydrolysis of the albumin salts increases as the dissociation constant of the added base diminishes. From the observations with amphoteric electrolytes it is found that variations of the basic dissociation constant between 10^{-12} and 10^{-15} have little effect on the formation of albumin ions in comparison with variations in the acid dissociation constant. Amphoteric electrolytes with small basic dissociation constant and higher acid dissociation constant are most favourable to the formation of neutral albumin complexes. H. M. D.

General Protein Chemistry. I. The Coagulation of Denatured Albumin, Considered as a Function of the Hydrogen Ion Concentration and of the Salts. Leonor Michaelis and Peter Rona (*Biochem. Zeitsch.*, 1910, **27**, 38—52).—Experiments were carried out to test the Helmholz-Bredig theory that surface-tension reaches a maximum and precipitation follows most readily when the protein particles carry no charge, that is, are immersed in a liquid of certain definite hydrogen ion concentration. For this purpose, dialysed albumin was denatured by heating. Mixtures of acetic acid and

sodium acetate in varying quantities were added to the turbid mixture, and the mixture producing the optimum sedimentation effect was noted. The hydrogen ion concentration of this solution could be readily determined. The rate of sedimentation varied when salts other than sodium acetate were employed. It was found that the isoelectric constant of serum albumin was $0{\cdot}3 \times 10^{-5}$, and the relative acidity $1{\cdot}6 \times 10^{3}$. The sedimentation rate is, in the first place, a function of the hydrogen ion concentration, and, in the second place, a function of the total content in electrolytes. The sedimentation rate is at a maximum when the $H^{\cdot}$ concentration is that of the isoelectric point, and is larger the poorer the solution is in total electrolytes.

S. B. S.

Hæmocyanin of Limulus polyphemus. Carl Alsberg and E. D. Clark (*J. Biol. Chem.*, 1910, 8, 1—8).—Hæmocyanin does not appear to be uniformly the same substance in all parts of the animal kingdom. That obtained from *Limulus* blood differs from that described by Henze from *Octopus* blood in percentage composition, in its precipitability by dialysis, by full saturation with magnesium sulphate, by half saturation with ammonium sulphate, in not having been crystallised, and in being more readily broken up by acid with liberation of the copper. No copper compound analogous to hæmatin was formed. In its globulin-like characters, the *Limulus* hæmocyanin thus resembles that described by Halliburton, who worked mainly with Crustacean blood. The following table of percentage composition is given:

	C.	H.	N.	S.	Cu.	O.
Octopus	53·66	7·33	16·09	0·86	0·38	21·68
Limulus	48·94	7·10	16·18	1·56	0·28	25·94

W. D. H.

Guanylic Acid. Ivar Bang (*Biochem. Zeitsch.*, 1910, 26, 293—311).—The protein was prepared by extracting pancreas with hot water and adding oxalic acid to the extract. This was dissolved in potassium hydroxide solution, and to this was added solid ammonium sulphate, so that the solution was $\frac{1}{2}$ to $\frac{2}{3}$ saturated (260 grams of salt to 500 c.c. of solution). The filtrate from the precipitated protein was diluted, and the guanylic acid precipitated from the liquid thus obtained either by copper acetate or copper sulphate and ammonia. The copper salt was decomposed by hydrogen sulphide, and the filtrate from the copper sulphide precipitated by 25% hydrochloric acid and twice the volume of alcohol. The precipitate was washed with water, and as the acid guanylic salt dissolved, acid was added to the washings. Four to five grams of guanylic acid were thus obtained from five organs of an ox. On hydrolysis, this guanylic acid yielded guanine, contaminated by a little xanthine, which the author succeeded in showing was a secondary product formed from the first-named base, phosphoric acid, and a pentose, the quantity of which was estimated by the author's hydroxylamine method, and amounted to 41% of the guanylic acid hydrolysed. The author discusses the formula of guanylic acid and its relationship to inosic and thymonucleic acids

S. B. S.

The Optical Rotation of Gelatin. Hans Trunkel (*Biochem. Zeitsch.*, 1910, 26, 493—513).—The optical activity of fresh gelatin solutions is variable, and reaches a maximum between the twelfth and hundred and twentieth hour. On warming, the original activity is restored. The activity is also dependent on temperature, decreasing with increasing temperature to 35°, when a maximum is attained. The optical activity is not proportional to the concentration; the weaker the concentration the smaller is the dextrorotation. The deviation is the smaller the longer and higher the solution is heated before taking the observation. The rotation of β-gelatin is appreciably smaller than that of the α-variety. The combining power for tannin of gelatin diminishes on keeping at first rapidly, and then more slowly; the rotatory power shows the opposite action (increasing rapidly at first, etc.). These phenomena are to be ascribed to a change in the condition known as "hysteresis," which the author discusses.

S. B. S.

The Anti-protease of Yeast Juice. Eduard Buchner and Hugo Haehn (*Biochem. Zeitsch.*, 1910, 26, 171—198).—It has been already shown that expressed yeast juice when kept loses first the co-enzyme and finally the zymase, which latter cannot be subsequently regenerated on addition of the former. The destruction of the zymase is due to an endotryptase. If boiled juice is added to the zymase, however, it can be preserved from destruction, owing to the fact that the boiled juice contains in addition to the co-enzyme an anti-protease which protects the coagulable proteins from the action of the endotryptase. This anti-protease also protects gelatin from liquefaction by endotryptase, and prevents the digestion of caseinogen by the same ferment. It acts also as an anti-substance to trypsin and pepsin. It is not identical with the co-enzyme, for the latter can be destroyed by heating yeast juice for several hours, or by the action of dilute acids at 100°, or by the action of alkali at 37°; under these conditions the anti-protease remains intact. The authors have not yet succeeded in separating chemically the anti-protease from the co-enzyme. Both are destroyed by lipase. The anti-protease is not a simple acid which inhibits the action of endotryptase, and as the anti-proteolytic action of the boiled juice remains intact after neutralisation, and neither is it a simple amino-acid, as substances do not exert any marked anti-action to endotryptase. Preliminary experiments indicate that it is an organic ester-like substance. The authors draw the conclusion that the anti-protease plays an important part in the life-processes of the yeast. The protective action is probably due to the capacity of the anti-protease to combine with the protein. S. B. S.

Organic Chemistry.

Catalytic Reactions in the Wet Way, Based on the Use of Aluminium Sulphate. Jean B. Senderens (*Compt. rend.*, 1910, 151, 392—394).—The addition of sand in the classical method for the preparation of ethylene is usually recommended on the ground that it prevents frothing. The present communication contains details of experiments from which it appears that this material acts as a catalyst and enables the reaction to proceed at a lower temperature. Aluminium sulphate, especially that prepared by calcining ammonium alum, is still more effective in this respect. The proportions recommended are 200 c.c. of a mixture of sulphuric acid (2 vols.), 95% alcohol (1 vol.), and 10 grams of anhydrous aluminium sulphate. Without the latter, the mixture yields no ethylene at 138°; with sand it gives 7·5—8 c.c. per minute, and with aluminium sulphate, 32 c.c. per minute.

The use of aluminium sulphate is stated to be advantageous in the industrial preparation of ethyl ether. A mixture of sulphuric acid (3 vols.) and 95% alcohol (4 vols.) with 5% of the sulphate gives ether at 110°, the reaction becoming rapid at 130°. In the absence of a catalyst the evolution of ether is not regular until 140°. The method is not suitable with the higher alcohols, the unsaturated hydrocarbon being produced together with liquid condensation products.

Propylene is conveniently prepared by heating propyl alcohol (4 vols.) with sulphuric acid (3 vols.) and 5% of anhydrous aluminium sulphate at 100—110°. The gaseous product contains 95% of propylene.

W. O. W.

Preparation of Glyceryl Mono- and Di-bromohydrins. P. Carré (*Bull. Soc. chim*, 1910, [iv], 7, 835—836).—Glyceryl α-bromohydrin, b. p. 134°/16 mm., is best prepared by diluting glycerol (200 grams) with water (60 grams), passing in hydrogen bromide (162 grams), warming the mixture in a closed vessel at 100° during five to six hours, and distilling the product under reduced pressure, the fraction boiling at 125—160°/16 mm. being collected and re-distilled. The αγ-dibromohydrin (b. p. 105°/16 mm.) is obtained in a yield of 55 to 60% of the theoretical by warming glycerol (185 grams) to 100°, passing in hydrogen bromide (325 grams), and heating the mixture at 100° during five to six hours. The fraction boiling at 100—120°/16 mm. is collected and re-distilled. Both products are colourless when freshly distilled, but become coloured on exposure to light.

T. A. H.

Solubility of Ethyl Ether in Water. Yukichi Osaka (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 21—35).—The ether used had b. p. 34·55°/761·2 mm. The relation between the refractive index and the composition of various mixtures of ether and water at 20° was first determined. It was found that the difference (Δ) between the angle of

refraction of water and the solution of ether in water is a linear function of the number of grams (x) of ether contained in 100 grams of the solution, as expressed by the formula $x = 0{\cdot}0946\Delta$.

In order to determine the solubility of ether in water at different temperatures, water was shaken with excess of ether in a tap funnel surrounded by a water jacket. When saturation was complete, the two layers were allowed to separate, and small portions of the lower layer run off into weighed quantities of water contained in stoppered flasks, the quantity of water being so regulated that a homogeneous solution was obtained at 20°. The weights of the separate portions of the lower layer were determined by difference. The angle of refraction of the homogeneous solution was then measured at 20°, and its composition determined by means of the formula given above; the composition of the saturated solution from which it was prepared could then be calculated.

The following results were obtained from the smoothed curve, x being the number of grams of ether dissolved in 100 grams of water in the saturated solution.

Temp. ...	0°	5°	10°	15°	20°	25°	30°
x	13·13	11·18	9·55	8·22	7·08	6·13	5·39

T. S. P.

Preparation of Chloroacetyl Chloride from Dichlorovinyl Ether. Consortium für Elektrochemische Industrie (D.R.-P. 222194).—When dichlorovinyl ether is saturated with dry hydrogen chloride, kept for twenty-four hours at the ordinary temperature, and then very gradually heated to boiling, *ethyl trichloroethyl ether*, $CH_2Cl{\cdot}CCl_2{\cdot}OEt$, is formed; this on distillation is readily decomposed into ethyl chloride and chloroacetyl chloride (b. p. 105°): $CHCl{:}CCl{\cdot}OEt + HCl \longrightarrow CH_2Cl{\cdot}CCl_2{\cdot}OEt \longrightarrow EtCl + CH_2Cl{\cdot}COCl$.

F. M. G. M.

Preparation of the Anhydrides of Fatty Acids from their Salts. Th. Goldschmidt (D.R.-P. 222236).—The preparation of aliphatic paraffin anhydrides by treating the salts of the acids with sulphur chloride has previously been described (Abstr., 1903, i, 309); it is now found that the reaction takes place if an intimate mixture of dry powdered sulphur and the sodium (or calcium) salt of the acid is treated with chlorine gas at a temperature of $-24°$ with continual stirring: $8C_2H_3O{\cdot}ONa + S + 6Cl = 6NaCl + Na_2SO_4 + 4(C_2H_3O)_2O$.

The mixture is then kept at the ordinary temperature, warmed to 90°, and subsequently distilled in a vacuum. F. M. G. M.

Preparation of β-Methyladipic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 221849).—The technical preparation of β-methyladipic acid may be conveniently carried out by oxidising 4-methyl*cyclo*hexanol with boiling concentrated nitric acid to 4-methyl*cyclo*hexanone; this intermediate product is then treated with potassium permanganate in alkaline solution, separated from hydrated manganese oxide, and the solution acidified, when a good yield of β-methyladipic

is obtained; it finds employment in the preparation of dyes and in pharmacology. F. M. G. M.

Preparation of Organic Aluminium Compounds. Ernst Schliemann's Export-Ceresin-Fabrik (D.R.-P. 221888).—Aluminium salts of mineral waxes may be obtained by treating the raw or purified waxes with aluminium salts, metallic aluminium, or aluminium hydroxide in the presence of an alkali, the function of which is to hydrolyse the esters of the fatty acids; the aluminium may combine with one, two, or three equivalents of the acid. A salt obtained from a pure wax containing 70% wax acid yielded an *aluminium montanate* of deep yellow colour, m. p. 93—95°, and giving a clear solution in hot petroleum. These compounds are employed as preservatives. F. M. G. M.

Preparation of Ammonium Hydrogen *l*-Tartrate. André Kling (*Bull. Soc. chim.*, 1910, [iv], 7, 774—776).—In connexion with the author's process for the estimation of tartaric acid as calcium racemate (this vol., ii, 359), a process for the preparation of ammonium hydrogen *l*-tartrate, based on the observations of Holleman (Abstr., 1898, i, 515; ii, 545) and Marckwald (Abstr., 1896, i, 207), is described. Ordinary tartaric acid is racemised by boiling it with sodium hydroxide solution, and the resulting racemic acid precipitated as the calcium salt. From this, racemic acid is regenerated, and the *l*-acid separated by means of cinchonine. From the cinchonine salt, the *l*-acid is recovered as ammonium hydrogen tartrate in the usual way, and freed from a trace of *d*-acid by fractional precipitation with calcium acetate, until the precipitate formed consists solely of crystals of calcium *l*-tartrate. The filtrate on concentration furnishes crystals of the desired salt. Illustrations of the crystals of calcium *l*-tartrate and racemate are given. T. A. H.

Ozo-salts of Titanium. Arrigo Mazzuchelli and Enrico Pantanelli (*Gazzetta*, 1910, 40, i, 666—682. Compare Abstr., 1909, i, 631).—The complex potassium ozotitanotartrate previously described (*loc. cit.*) crystallises with $9H_2O$, not with $10H_2O$, as there stated owing to a printer's error in the original paper. R. V. S.

Preparation of Acraldehyde. Jean B. Senderens (*Compt. rend.*, 1910, 151, 530—532. Compare this vol, i, 649).—Anhydrous or hydrated aluminium sulphate effects the catalytic dehydration of glycerol at 105—110°, producing acraldehyde. The large amount of potassium hydrogen sulphate commonly employed in the preparation of this substance from glycerol is unnecessary, since the salt acts as a catalyst. By heating 250 grams of glycerol with 10 grams of potassium hydrogen sulphate for three hours at a temperature not exceeding 110°, 130—140 c.c. of liquid are obtained, which, on re-distillation, furnishes 34—38 c.c. of acraldehyde. The yield is somewhat smaller than that obtained in the usual way, but the product is more stable, and polymerises less rapidly. W. O. W.

Action of Acetic Anhydride and Its Homologues on Organo-magnesium Compounds. H. Fournier (*Bull. Soc. chim.*, 1910, [iv], 7, 836—840).—Grignard and Tissier have shown (Abstr., 1901, i, 316) that tertiary alcohols are formed by the action of acetic or benzoic anhydride on magnesium methyl iodide. The author has found, in addition, that ketones are produced in this reaction (*Bull. Soc. chim.*, 1904, [iii], 31, 483; 1906, [iii], 35, 19), and a detailed account of his results are now given.

The anhydride (1 mol.) is dissolved in ether, and to this the magnesium alkyl haloid (1 mol.) is added drop by drop, the mixture being cooled in a bath of ice and salt and continuously agitated. The mixture is set aside during two to three hours, and then poured into ice-cold water. The ethereal extract of this is then shaken with dilute sodium hydroxide solution. The purified ethereal solution contains (1) the ketone formed, (2) the ester corresponding to the acid anhydride employed, and the alkyl radicle of the magnesium compound used, and (3) sometimes the tertiary alcohol. The last is separated by fractional distillation, and the ester is eliminated from the residue by hydrolysis, the alcohol formed being distilled off. The ketone is finally isolated by adding water, extracting with ether, drying the solution, and fractionating. The chief reactions occurring are represented by the following equations: $(R\cdot CO)_2R + R'MgBr = R\cdot CO\cdot O\cdot CRR'\cdot O\cdot MgBr + H_2O = MgBr\cdot OH + R\cdot CO_2H + R\cdot CO\cdot R'$.

With magnesium ethyl bromide, acetic anhydride yields methyl ethyl ketone; with magnesium *iso*butyl chloride, methyl *iso*butyl ketone, and with magnesium *iso*amyl bromide, methyl *iso*amyl ketone. The reaction has also been investigated for propionic, butyric, *iso*butyric, *iso*propylacetic, and heptoic anhydrides with various magnesium alkyl haloids, and the corresponding ketones prepared and identified, usually by means of their semicarbazones. T. A. H.

Preparation of Methylene Ketones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 222551).—The action of formaldehyde on ketones in the presence of alkaline condensing agents yields keto-alcohols, which by the action of condensing agents, such as zinc chloride, sulphuric acid, or sodium hydrogen sulphate, are converted into methylene ketones.

Methyleneacetone, $COMe\cdot CH{:}CH_2$, b. p. 80°, under the ordinary pressure is prepared by heating ketobutanol (100 parts) with zinc chloride (2 parts). It is a colourless, highly refractive oil with a pungent odour.

Methylenemethyl ethyl ketone, $CH_2{:}CH\cdot COEt$, a colourless oil with a strong odour, b. p. 96°, is similarly prepared. These compounds are employed in pharmacy. F. M. G. M.

Action of Ultra-violet Light on Certain Carbohydrates. Henri Bierry, Victor Henri, and Albert Ranc (*Compt. rend.*, 1910, 151, 316—318).—Under the influence of light from a quartz-mercury lamp, lævulose undergoes profound decomposition when in aqueous solution, carbon monoxide, carbon dioxide, formaldehyde, and methyl alcohol having been recognised amongst the products. The reaction proceeds more readily in a vacuum than when air is present.

Aldoses do not appear to undergo this degradation. Glycerol and mannitol after exposure to the rays acquire reducing properties.
W. O. W.

Degradation Experiments with Carbohydrates. Carl Neuberg and Else Hirschberg (*Biochem. Zeitsch.*, 1910, 27, 327—338).—Attempts were made to prepare *l*-glyceraldehyde. The method employed was to degrade *l*-arabonic acid to *l*-erythrose by the ferric acetate and hydrogen peroxide method of Ruff and Meusser, to oxidise the latter to *l*-erythronic acid by bromine water, and to obtain *l*-glyceraldehyde from the latter both by the ferric acetate and hydrogen peroxide oxidation, and by Neuberg's method by the electrolytic decomposition of the copper salt. The experiments were made possible by the authors' discovery of an easy method for preparing *l*-arabonic acid. Cherry gum was hydrolysed by diluto sulphuric acid, which was then removed. The *l*-arabinose thus formed was not isolated, but the quantity in solution was directly estimated polarimetrically, and then sufficient bromine was added to oxidise it to *l*-arabonic acid, which was then isolated as a calcium salt. On oxidising this to *l*-erythrose, an acid by-product insoluble in alcohol was isolated, and obtained in the form of a brucine salt, which was apparently *l*-$\alpha\beta\gamma$-trihydroxybutyrylformic acid, $CO_2H{\cdot}CO{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$. On attempting to prepare *l*-glyceraldehyde from erythronic acid by both methods mentioned, an analogous *l*-$\alpha\beta$-dihydroxypropionylformic acid was also probably formed. Only traces of a glyceraldehyde could be isolated, however, and this was optically inactive. S. B. S.

Influence of Boric Acid on the Inversion of Sucrose by the Catalytic Action of Hydrochloric Acid. Katsunosuke Arafuru (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 229—236).—Boric acid acts as a positive catalyst on the inversion of sucrose. Löwenthal and Lenssen (*J. pr. Chem.*, 1862, 85, 401) found that it retards the catalytic action of hydrochloric acid, but the author finds that it increases the catalytic action. When the concentration of the hydrochloric acid is kept constant, the accelerating effect of the boric acid increases with its concentration, whereas the influence of the boric acid on the catalytic action of hydrochloric acid is practically independent of the concentration of the latter acid. T. S. P.

Constitution of Vicianose: Diastatic Hydrolysis. Gabriel Bertrand and Gustave Weisweiller (*Compt. rend.*, 1910, 151, 325—327. Compare this vol., i, 156).—Vicianose, the new sugar from *Vicia angustifolia*, has been hydrolysed by emulsin, and found to furnish dextrose and arabinose in equimolecular proportions. It may therefore be regarded as a disaccharide formed by the union of these two substances. W. O. W.

New Observations on Callose. Louis Mangin (*Compt. rend.*, 1910, 151, 279—283. Compare Abstr., 1890, i, 734).—The tissue of *Bornetina corium*, a coriaceous cryptogram, is a substance having the same composition as cellulose, but differing from it in its insolubility in

Schweitzer's reagent and its behaviour towards iodine. Sulphuric acid hydrolyses it with formation of dextrose. From these and other observations the author considers it to consist of practically pure callose.

Like cellulose, callose is met with in different states of aggregation, probably corresponding with different degrees of polymerisation. Tanret's fongose (Abstr., 1898, i, 154) is supposed to be identical with callose. W. O. W.

Relations of Callose with Fongose. Charles Tanret (*Compt. rend.*, 1910, 151, 447—449. Compare preceding abstract).—The author denies the identity of callose with fongose (fungose). Callose is insoluble in aqueous alkali hydroxides, but becomes soluble after treatment with dilute sulphuric acid, as described in connexion with the preparation of fongose. Callose appears to be a more complex substance than fongose, and the relation between the two compounds appears to be similar to that existing between starch and amylose. W. O. W.

Celluloses. I. William Oechsner de Coninck and A. Raynaud (*Bull. Acad. roy. Belg.*, 1910, 587—589).—On macerating filter paper with concentrated hydrochloric acid at 28°, no reducing substance is produced even after forty hours. If the paper is macerated during sixty-two hours and the mixture then heated at 95—96° during twenty minutes, it becomes brown, but the filtrate does not reduce Fehling's solution. The brownish residue is partly soluble in ammonia, and consists of humic matter. Cotton macerated during forty hours in hydrochloric acid shows no reduction, but after eighty-seven hours at 28·5°, and then ten minutes at 95—96°, shows copious reduction. It dissolves in fuming hydrobromic acid at 29° in a few minutes, and the solution blackens on keeping. Such a solution gives a slight, brownish-black precipitate, partly soluble in ammonia on dilution, and reduces Fehling's solution. T. A. H.

Cellulose. I. Hydrocellulose. H. Jentgen (*Zeitsch. angew. Chem.*, 1910, 23, 1541—1546).—Hydrocellulose is formed by the action of water vapour on cellulose containing adsorbed acid, the acid acting as a contact catalyst. For the formation of the adsorption product between acid and cellulose, it is necessary that the former be in the so-called molecular condition, that is, dissolved in a non-dissociating medium, such as glacial acetic acid, amyl acetate, ether, etc. The acids generally used are hydrochloric and sulphuric, and also their salts with weak bases, and the velocity of hydrolysis depends on the medium used, of which glacial acetic acid is the best.

Hydrocellulose is not extremely resistent towards acids and bases. At medium concentrations, sulphuric acid causes amyloid formation, stronger acid dissolves it, and the most concentrated acid destroys it. It is soluble in zinc chloride, phosphoric acid, fuming nitric acid, and concentrated ammoniacal copper oxide, in the last-named to 10—15%; it is only very sparingly soluble in Wright's liquid.

Alkalis readily attack hydrocellulose, oxycellulose being formed at

the boiling point. It dissolves in cold sodium hydroxide to the extent of about one-third, the remainder being mercerised. The solution contains hemi-cellulose, which can be precipitated by acids, and also yellow to brown degradation products, which are soluble in water.

T. S. P.

Colloidal Properties of Starch, Especially its Electrical Transport. Filippo Bottazzi and C. Victoroff (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 7—14. Compare Fouard, Abstr., 1908, i, 953; Maquenne and Roux, *ibid.*, 1906, i, 547).—The authors confirm the results of the above-named writers. The amylose of starch forms a colloidal solution with water, which is perfectly clear and transparent, but does not dialyse. The solution can be filtered through hardened gelatin under pressure (ultra-filtration). When an electric current is passed through it, no migration is observed. The amylopectin of starch forms with water a suspension, in which the granules are visible under the ultra-microscope. The suspension is the more stable the more alkali it contains, so that dialysis, which removes a part of the alkali, causes a partial precipitation. The solution is precipitated by acids. When subjected to ultra-filtration, the substance does not pass through the gelatin, and thus a separation from amylose can be effected. The two substances can also be separated by precipitating the amylopectin with acid, the amylose being afterwards thrown down by the addition of alcohol to the filtrate. Amylopectin is transported towards the anode in neutral solutions containing only small quantities of electrolytes; when large quantities of the latter are present, or when the solution is alkaline or acid, no transport takes place.

R. V. S.

Action of (1) Hydracids, (2) Hydrolysing Agents, on Starch. William Oechsner de Coninck (*Bull. Acad. roy. Belg.*, 1910, 515—517, 586—587).—A mixture of starch (3 grams), water (35—40 grams), and concentrated hydrochloric acid (2 c.c.) kept at 14° reduces Fehling's solution slightly after three days and markedly after six days. The action is much more rapid at 100°. Concentrated hydrobromic or hydriodic acid behaves similarly on being kept in contact with starch at the ordinary temperature, and hydrolysis is also effected by hot dilute hydriodic acid.

The following substances dissolved, or suspended, in water also hydrolyse starch: ferric, platinic, auric, and stannous chlorides; chlorine; potassium ferrocyanide, ferricyanide, dichromate, and hydroxide; sodium hydroxide, hydrogen carbonate, and dichromate; ammonium, lithium, barium, strontium, and calcium hydroxides; cupric sulphate; cobalt nitrate; nitric (dilute), chromic (dilute), acetic, tartaric, benzoic, picric, and other organic acids.

T. A. H.

Synthesis of Agmatine. Albrecht Kossel (*Zeitsch. physiol. Chem.*, 1910, 68, 170—172. Compare this vol., i, 500).—Agmatine has been synthesised by the following process. Carbon dioxide is passed for fourteen days through a suspension of silver cyanamide in a

solution of tetramethylenediamine hydrochloride. The liquid is acidified with sulphuric acid, filtered, and the filtrate mixed with an aqueous solution of silver sulphate until a test portion gives a dark brown precipitate with barium hydroxide. The whole is then neutralised with barium hydroxide, filtered, and the filtrate saturated with barium hydroxide. The dark brown precipitate is washed with water, suspended in dilute sulphuric acid, decomposed with hydrogen sulphide, and the resulting sulphate transformed into the sparingly soluble carbonate.

Agmatine can also be obtained by the direct action of an aqueous solution of cyanamide on tetramethylenediamine, and its constitution as aminobutyleneguanidine, $NH_2 \cdot C(NH) \cdot NH \cdot [CH_2]_4 \cdot NH_2$, is confirmed. J. J. S.

Attempts to Synthesise αε-Diaminopentan-γ-ol. Otto Morgenstern and Ernst Zerner (*Monatsh.*, 1910, 31, 777—780).—With the object of preparing large quantities of αε-diaminopentan-γ-ol, it was sought to convert *s*-dichlorohydrin by means of potassium cyanide into the dinitrile, $OH \cdot CH(CH_2 \cdot CN)_2$, and reduce this compound. Dichlorohydrin (1 mol.) and potassium cyanide (2 mols.) were caused to interact in various ways, but the nitrile was only obtained as a blackish-brown, amorphous, hygroscopic solid, which could not be purified. On hydrolysis, glutaconic acid was obtained, of which the *copper* salt forms a bluish-green, crystalline powder, becoming brown at 250°. Reduction of the crude nitrile by means of sodium and amyl alcohol gave a small quantity of a colourless distillate with an amine-like odour, b. p. 255—270°. *Diaminopentanol picrate*, $C_5H_{14}ON_2,2C_6H_3O_7N_3$, decomposes at 272°. E. F. A.

Synthesis of Polypeptides. XXXII. (I) Derivatives of Aspartic Acid. Emil Fischer and Albert Fiedler (*Annalen*, 1910, 375, 181—198. Compare Abstr., 1909, i, 887).—In view of the importance of aspartic acid as a constituent of natural proteins, the authors have applied to it the reactions by which glycylglutamyldiglycine was synthesised from glutamic acid (Fischer, Kropp and Stahlschmidt, Abstr., 1909, i, 368), and have succeeded in preparing a tetrapeptide from 3 mols. of glycine and 1 mol. of aspartic acid, to which the name *glycylaspartyldiglycine* is assigned.

Chloroacetyl-l-*aspartic acid*, $CH_2Cl \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, prepared from chloroacetyl chloride and aspartic acid or asparagine under suitable conditions, is a crystalline powder, which has m. p. 142—143° (decomp., corr.), and $[\alpha]_D^1$ 4·19° in aqueous solution, and yields with 25% ammonium hydroxide after three days at the ordinary temperature, *glycyl*-l-*aspartic acid*, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, m. p. 207° (decomp., corr.), $[\alpha]_D^{20}$ 11·08° in aqueous solution, which crystallises with $1H_2O$. d-α-*Bromoisohexoylglycyl*-l-*aspartic acid*, $CHMe_2 \cdot CH_2 \cdot CHBr \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, prepared from glycyl-*l*-aspartic acid and *d*-α-bromo*iso*hexoyl chloride, is hygroscopic, has m. p. 119—120° (corr.), $[\alpha]_D^{21}$ 61·35° in alcoholic solution, separates from hot water in short prisms containing $\frac{1}{2}H_2O$,

and by treatment with ammonium hydroxide as above is converted into l-*leucylglycyl*-l-*aspartic acid*,
$CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$,
m. p. 239° (decomp., corr.), and $[\alpha]_D^{20}$ 55·10° in aqueous solution.

Chloroacetylaspartic acid is treated with acetyl chloride and phosphorus pentachloride in the cold, and an ethereal solution of the resulting crude acid chloride is treated with ethereal ethylglycine at 0°, whereby ethylglycine hydrochloride and *ethyl chloroacetylaspartyldiglycine*,
$CH_2Cl \cdot CO \cdot NH \cdot CH(CO \cdot NH \cdot CH_2 \cdot CO_2Et) \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$,
are obtained; after the removal of the former by cold water, the latter is purified by hot ethyl acetate and animal charcoal. It separates in colourless needles, has m. p. 176—177° (corr.), and is optically inactive, racemisation having occurred probably during the conversion of the chloroacetylaspartic acid into its chloride. *Chloroacetylaspartyldiglycine*, m. p. 142—143° (decomp., corr.), obtained by hydrolysing the preceding ester with *N*-sodium hydroxide at the ordinary temperature, separates from hot water in crystals containing H_2O, is sparingly soluble in cold water, has a strongly acid reaction, and is converted by 25% ammonium hydroxide at 25° in five days into *glycylaspartyldiglycine*,
$NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO \cdot NH \cdot CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$,
m. p. 201—203° (corr.), an aqueous solution of which becomes dark blue when boiled with copper oxide.

d-*α*-*Bromoisohexoyl*-l-*aspartic acid*,
$$CHMe_2 \cdot CH_2 \cdot CHBr \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H,$$
m. p. 150° (corr.), $[\alpha]_D^{22}$ 8·10° in aqueous solution, is prepared from aspartic acid and *d*-*α*-bromo*iso*hexoyl chloride, and is converted by ammonium hydroxide into l-*leucyl*-l-*aspartic* acid, m. p. 182° (decomp., corr.), $[\alpha]_D^{18}$ 26·92° in aqueous solution, which separates from hot water in slender needles containing $2H_2O$. C. S.

Synthesis of Polypeptides. XXXII. (II.) Dipeptides of Serine. Emil Fischer and Hans Roesner (*Annalen*, 1910, 375, 199—206).—As mixed polypeptides of serine are probably formed by the partial hydrolysis of silk-fibroin, the authors have prepared certain dipeptides of serine which it is hoped may be of use in elucidating the nature of the hydrolytic products of silk-fibroin. The reaction between *r*-serine and chloroacetyl chloride in *N*-sodium hydroxide cooled by a freezing mixture leads to the formation of *chloroacetylserine*,
$$CH_2Cl \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot OH,$$
m. p. 122—123° (corr.), which tastes and reacts strongly acid, and is converted by 25% ammonium hydroxide at the ordinary temperature into *glycyl*-dl-*serine*, m. p. 207° (decomp., corr.), which has a slight acid reaction and gives a deep blue colour when its aqueous solution is warmed with copper oxide. *Glycyl*-dl-*serine anhydride*,
$$OH \cdot CH_2 \cdot CH\langle \begin{matrix} NH \cdot CO \\ CO \cdot NH \end{matrix} \rangle CH_2,$$
m. p. 227° (corr.), is obtained by saturating a cold methyl-alcoholic suspension of glycylserine with hydrogen chloride and treating the

product in concentrated methyl-alcoholic solution with methyl alcohol saturated with ammonia at 0°.

By similar methods, *α-bromopropionylserine*,

$$CHBrMe\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot OH,$$

m. p. 143° (decomp., corr.), *i-alanylserine*,

$$NH_2\cdot CHMe\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot OH,$$

m. p. 209—214° (decomp., corr.), and *i-alanylserine anhydride*,

$$OH\cdot CH_2\cdot CH\langle \begin{matrix} NH\cdot CO \\ CO\cdot NH \end{matrix} \rangle CHMe,$$

m. p. 228° (corr.), have been obtained. C. S.

Syntheses of Hydroxybetaines. I. Synthesis of β-Trimethyl-α-lactobetaine. Adolf Rollett (*Zeitsch. physiol. Chem.*, 1910, **68**, 1—11).—Attempts have been made to synthesise hydroxybetaines, as compounds of this type, for example, carnitine, novaine, reducto-novaine, and oblitine, occur in nature.

The *basic hydriodide* of *β-trimethyl-α-lactobetaine*, $C_{12}H_{27}O_6N_2I$, is formed when *iso*serine (Fischer and Leuchs, Abstr., 1902, i, 269) is dissolved in a 7·5% solution of sodium hydroxide in methyl alcohol, mixed with methyl iodide, and the resulting sodium salt decomposed with hydriodic acid. It crystallises from 96% alcohol in compact, transparent prisms, m. p. 198—200°. The *sodium* salt,

$$C_{12}H_{26}O_6N_2INa,$$

crystallises from 96% alcohol in slender, glistening needles, m. p. 203—206°. The basic *hydrochloride*, $C_{12}H_{27}O_6N_2Cl$, obtained by the action of silver chloride on an aqueous solution of the hydriodide, crystallises in slender needles, m. p. 200°. The normal *hydriodide*, $C_6H_{14}O_3NI$, has m. p. 78—80°, and when crystallised from alcohol yields the basic salt. The normal *hydrochloride*, $C_6H_{14}O_3NCl$, has m. p. 155—158°; the *platinichloride*, $C_{12}H_{28}O_6N_2PtCl_6$, crystallises from 50% alcohol. *β-Trimethyl-α-lactobetaine*,

$$NMe_3\langle \begin{matrix} CH_2\cdot CH\cdot OH \\ O---CO \end{matrix},$$

forms hygroscopic needles, m. p. 203° (decomp.).

The *platinichloride* of the ethyl ester,

$$[NMe_3Cl\cdot CH_2\cdot CH(OH)\cdot CO_2Et]_2PtCl_4,$$

crystallises from aqueous alcohol in hexagonal prisms, which decompose at 235°.

Trimethylamine and β-chlorolactic acid yield carbon dioxide, acetaldehyde, and trimethylamine hydrochloride. J. J. S.

Cheirolin, the Thiocarbimide in Wall-flower Seeds. Its Synthesis and Degradation. Wilhelm Schneider (*Annalen*, 1910, **375**, 207—254. Compare Abstr., 1909, i, 118, 826).—A better method than Wagner's (Abstr., 1908, i, 202) for the isolation of cheirolin from wall-flower seeds is described. The finely ground seeds are extracted with ether, which removes the greater part of the oily constituents, but only a trace of cheirolin. The seeds are then covered with ether, and shaken with 5% sodium carbonate. The cheirolin is thereby liberated and dissolved by the ether. The ethereal extract is evaporated, and the residue is dissolved in 0·5%

sulphuric acid at 50—60°; the acid solution, after being filtered, is treated with ammonium sulphate, the cheirolin is extracted with ether, and is obtained almost pure by evaporating the ethereal solution after it has been dried with potassium carbonate. The seeds of *Cheiranthus cheiri* yield 1·6—1·7%, and those of *Erysimum arkansanum*, 1·3%.

Cheirolin, $C_5H_9O_2NS_2$, m. p. 47—48°, b. p. 200°/3 mm., separates from ether in large, colourless, odourless, prismatic plates, $a:b:c = 0{\cdot}9418:1:0{\cdot}6228$. Wagner (*loc. cit.*) described it as an alkaloid, but it is entirely without basic properties. The two atoms of sulphur have different functions in the molecule, one being easily oxidised to sulphuric acid, the other only with difficulty. The decomposition of cheirolin by warm dilute acids or alkalis is that of a thiocarbimide, hydrogen sulphide, carbon dioxide, and a primary base, $C_4H_{11}O_2NS$, being obtained quantitatively. This supposition is confirmed, not only by the formation of thiocarbamides with ammonia and amines, but also by the production of the same thiocarbamide from cheirolin and aniline, and from phenylthiocarbimide and the base, $C_4H_{11}O_2NS$; by desulphurisation with mercuric oxide, this thiocarbamide yields a carbamide identical with Wagner's cheirol. The base, $C_4H_{11}O_2NS$, does not contain hydroxyl; the presence of a sulphone group is indicated by the firmness with which the sulphur is bound, the saturated character and insolubility in ether of the base, its stability to hydrochloric acid at 200°, hydriodic acid, and cold potassium permanganate. Boiling potassium permanganate converts the base into an acid, $C_3H_7O_2S{\cdot}CO_2H$, and fuming nitric acid at 200° produces a good yield of methylsulphonic acid; these two reactions indicate the presence of $\cdot CH_2{\cdot}NH_2$ and of ·SMe respectively. Consequently, the base is probably

$$SO_2Me(C_2H_4){\cdot}CH_2{\cdot}NH_2,$$

and cheirolin a methylsulphone derivative of propylthiocarbimide, $SO_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NCS$, the methylsulphone group being in the γ-position because the substance is optically inactive. The correctness of these views has been proved synthetically. *Methyl-γ-bromopropylsulphone*, $SO_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$, m. p. 34°, b. p. 156—158°/1 mm., obtained by treating an alcoholic solution of sodium methylmercaptide at 0° with an alcoholic solution of αγ-dibromopropane and oxidising the resulting sulphide with potassium permanganate, is converted by potassium thiocyanate into the *thiocyanate*,

$$SO_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SCN,$$

m. p. 57°, but all attempts to convert it into the isomeric thiocarbimide have been unsuccessful. The synthesis of cheirolin has been achieved therefore by the following process. *Methyl γ-phthaliminopropyl sulphide*, $C_6H_4{<}\overset{CO}{\underset{CO}{>}}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SMe$, m. p. 59—60°, obtained from alcoholic sodium methylmercaptide and γ-bromopropylphthalimide, yields by hydrolysis *methyl γ-aminopropyl sulphide*, b. p. 170° (*hydrochloride*, m. p. 136°; *oxalate*, decomp. 208°; *picrate*, m. p. 126—127°; *picrolonate*, m. p. 184—185°), the hydrochloride of which is oxidised, best by permanganic acid, to *methyl γ-aminopropylsulphone*, the derivatives of which are identical with those of the primary base obtained by the hydrolysis of cheirolin; for

example, the *hydrochloride*, m. p. 146°, *platinichloride*, decomposing at 234°, *di-γ-methylsulphonepropylthiocarbamide*, m. p. 125—126°. The synthetic methyl γ-aminopropylsulphone is finally converted into cheirolin by Hofmann's method with carbon disulphide.

The following compounds have also been prepared: Methyl γ-aminopropylsulphone forms, in addition to the derivatives mentioned above, a *picrate*, m. p. 190—192°, *picrolonate*, m. p. 216°, an N-*benzoyl* derivative, m. p. 102°, is oxidised by boiling potassium permanganate to *methylsulphonepropionic acid*, $SO_2Me\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 105°, and is converted by an excess of methyl iodide into *trimethyl-γ-methylsulphonepropylammonium iodide*, $SO_2Me\cdot[CH_2]_3\cdot NMe_3I$, m. p. 150—152°. Methyl γ-aminopropyl sulphide reacts with an alcoholic solution of cheirolin to form the *thiocarbamide*,

$$SMe\cdot[CH_2]_3\cdot NH\cdot CS\cdot NH\cdot[CH_2]_3\cdot SO_2Me,$$

m. p. 59°, with alcoholic carbon disulphide to form ultimately *di-γ-methylthiopropylthiocarbamide*, $CS[NH(CH_2)_3\cdot SMe]_2$, m. p. 55—56°, and with sodium methoxide and an excess of methyl iodide to form the NS-*dimethiodide* of methyl γ-dimethylaminopropylsulphide,

$$CH_3\cdot S(MeI)\cdot[CH_2]_3\cdot NMe_3I,$$

decomposing at 246°, and also the N-*methiodide*, decomposing at 217°.

An alcoholic solution of cheirolin is converted by alcoholic ammonia into *γ-methylsulphonepropylthiocarbamide*,

$$SO_2Me\cdot[CH_2]_3\cdot NH\cdot CS\cdot NH_2,$$

m. p. 116°, by alcoholic aniline into *γ-methylsulphonepropylphenylthiocarbamide*, $SO_2Me\cdot[CH_2]_3\cdot NH\cdot CS\cdot NHPh$, m. p. 136° (which is also obtained from phenylthiocarbimide and methyl γ-aminopropylsulphone), and by alcoholic methyl γ-aminopropylsulphone into s-*di-γ-methylsulphonepropylthiocarbamide*, $CS(NH\cdot[CH_2]_3\cdot SO_2Me)_2$, m. p. 125—126°, which is also obtained by desulphurising an aqueous solution of cheirolin at 50—60° with mercuric oxide ($\frac{1}{2}$ mol.). s-*Di-γ-methylsulphonepropylcarbamide*, m. p. 172°, is obtained by the action of mercuric oxide on the preceding thiocarbamide, or of an excess of mercuric oxide on a boiling aqueous solution of cheirolin. C. S.

Effect of Pressure and Temperature on Cyanogen. E. Briner and A. Wroczynski (*Compt. rend.*, 1910, **151**, 314—316. Compare this vol., ii, 557, 707).—The conversion of cyanogen into paracyanogen, which takes place at about 310° under ordinary pressure, can be brought about at lower temperatures by increasing the pressure; thus, at 220° and 300 atmospheres, the gas undergoes a diminution in volume of 10%, and then contains 16% of free nitrogen. Polymerisation also occurs in the neighbourhood of the critical temperature and pressure, but probably not with sufficient rapidity to vitiate determinations of these constants. W. O. W.

Formation of *o*-Nitrotoluene from 2:4-Dinitrotoluene. Moritz Kohn (*Monatsh.*, 1910, **31**, 745—746. Compare Abstr., 1909, i, 561).—*o*-Nitrotoluene is formed by boiling 2:4-dinitrotoluene with an aqueous alkaline solution of hydroxylamine. No trace of the formation of *p*-nitrotoluene could be detected. E. F. A.

Dinitro-*p*-xylenes. Jan J. Blanksma (*Chem. Weekblad*, 1910, 7, 727—730).—Preparation of the three isomeric nitro-*p*-xylenes by an indirect method has established the fact that it is possible to separate the pure compounds from the mixture resulting from the nitration of *p*-xylene, although only a small proportion of the 2 : 3- and 2 : 5-compounds is obtained.

On reduction with ammonium sulphide, 2 : 3-dinitro-*p*-xylene yields *p*-xylidine-3-sulphonic acid, probably due to replacement of one nitro-group by SH, followed by intramolecular oxidation and the addition of one molecule of water. A. J. W.

Higher Homologues of Benzene. Erling Schreiner (*J. pr. Chem.*, 1910, [ii], 82, 292—296).—The following compounds are produced by the Grignard and the Friedel-Craft reactions. *β*-Chloro-*β*-methylpentane, b. p. 110—113°, D_4^{15} 0·8678, $n_D^{16·5}$ 1·41476, yields with benzene and aluminium chloride *β-phenyl-β-methylpentane*, $CMe_2Pr^{\alpha}Ph$, b. p. 205—206°, D_4^{19} 0·8796, $n_D^{18·5}$ 1·49554. *β-Chloro-βδ-dimethylpentane*, $CHMe_2{\cdot}CH_2{\cdot}CMe_2Cl$, b. p. 126—127°, D_4^{19} 0·8650, $n_D^{16·5}$ 1·42015, prepared from the corresponding carbinol, is converted into *β phenyl-βδ-dimethylpentane*, b. p. 218°, D_4^{15} 0·8741, $n_D^{16·5}$ 1·49383. γ-Chloro-γ-methylpentane, b. p. 116°, D_4^{14} 0·8893, $n_D^{16·5}$ 1·42315, yields *γ-phenyl-γ-methylpentane*, b. p. 204—206°, D_4^{15} 0·8773, $n_D^{16·5}$ 1·49724. Triethylcarbinol forms *γ-chloro-γ-ethylpentane*, CEt_3Cl, b. p. 143—144°, D_4^{25} 0·8644, n_D^{25} 1·43276, which is converted into *γ-phenyl-γ-ethylpentane*, b. p. 220—222°, D_4^{25} 0·8656, n_D^{25} 1·49211. C. S.

The Ditolylmethane from Formaldehyde and Toluene. Otto Fischer and Hans Gross (*J. pr. Chem.*, 1910, [ii], 82, 231—237).—The large residue obtained in the preparation of ditolylmethane from methylal or paraformaldehyde and toluene (Abstr., 1909, i, 563) yields *β*-methylanthracene by further distillation. When the residue is distilled under diminished pressure, it yields a further quantity of ditolylmethane and a mobile, colourless liquid with a feeble, blue fluorescence, b. p. 247—250°/12 mm., which is apparently a polymeride of ditolylmethane. When the condensation of toluene and paraformaldehyde or methylal in the presence of sulphuric acid is performed at −15° to −10°, only a little ditolylmethane is obtained, the chief product being an amorphous powder.

The ditolylmethane obtained by the authors' process (and also that prepared by Weiler's method) must contain a little *op*-ditolylmethane, because it does not solidify in ice and salt, melts at −3°, and yields *β*-methylanthracene by distillation over pumice in a red-hot tube; the pure dipara-substance solidifies in ice and salt, melts at 22—23°, and does not yield *β*-methylanthracene on distillation.

The dinitroditolylmethane obtained by Weiler by the nitration of ditolylmethane is identical with that prepared from *o*-nitrotoluene, formaldehyde, and concentrated sulphuric acid, and must therefore be 3 : 3′-dinitrodi-*p*-tolylmethane; by reduction, it yields the corresponding *diamino*-compound, $C_{15}H_{18}N_2$, m. p. 72—74°, which forms a *diacetyl* derivative, m. p. 264°. C. S.

Ditolylethane and Ditolylethylene from Paraldehyde and Toluene. Otto Fischer and L. Castner (*J. pr. Chem.*, 1910, [ii], 280—288).—Continuing a former research (O. Fischer, this Journ., 1875, 154), the authors show that the best condition for the production of ditolylethane is to add slowly paraldehyde to a vigorously stirred mixture of concentrated sulphuric acid and toluene at $-20°$, the temperature being kept below $-15°$; after three to four hours the temperature is slowly increased to 0°, and the mass added to water at 0°. When cold toluene is added to a mixture of pure sulphuric acid and paraldehyde at $-20°$, and after three to four hours the temperature is raised to 10° and the mass poured into water, the ditolylethane contains 25—33% of di-*p*-tolylethylene, which is separated by fractional distillation. The di-*p*-tolylethylene and the di-*p*-tolylethane obtained from it by reduction with sodium and alcohol do not yield *β*-methylanthracene when passed over pumice in a red-hot tube. By bromination in carbon disulphide at 0°, di-*p*-tolylethylene yields an unstable additive compound, which loses hydrogen bromide during its purification, *ω bromodi*-p-*tolylethylene*, $C_{16}H_{15}Br$, m. p. 53—54°, being obtained.

The formation of di-*p*-tolylethylene may be due to the intermediate production of crotonaldehyde, since under the conditions mentioned above this aldehyde, toluene, and sulphuric acid produce the unsaturated hydrocarbon. C. S.

Action of Iodine on *m*-Toluidine. Henry L. Wheeler (*Amer. Chem. J.*, 1910, **44**, 126—145).—It has been shown by Wheeler and Liddle (this vol., i, 17, 19) that when *p*-toluidine is treated with iodine, both mono- and di-iodo-derivatives are produced, whilst with *o*-toluidine, the mono-derivative only is obtained. A study has now been made of the behaviour of *m*-toluidine towards iodine, and the 6-iodo-, 4 : 6-di-iodo-, and 2 : 4 : 6-tri-iodo-derivatives have been isolated. It is probable that small quantities of isomeric compounds, such as the 4-iodo- and 2 : 6-di-iodo-derivatives, are also formed. When *m*-toluidine (1 mol.) is mixed with iodine (two or three atoms) in presence of ether, water, and calcium carbonate, the product consists of mono- and di-iodo-toluidines, together with some of the original base. When the proportion of iodine is increased to four atoms, a mixture of the mono-, di-, and tri-iodo-derivatives is obtained, in which the di-derivative predominates, whilst with six atoms of iodine, tri-iodo-*m*-toluidine and resinous material are produced.

[With Charles Hoffman.]—6-Iodo-*m*-toluidine has m. p. 37—39°, instead of 98—99° as stated by Artmann (Abstr., 1905, i, 879). *6-Iodo-3-acetylaminobenzoic acid*, $NHAc{\cdot}C_6H_3I{\cdot}CO_2H$, m. p. 210°, obtained by the oxidation of 6-iodoaceto-*m*-toluidide with potassium permanganate, forms long, colourless, prismatic needles. An attempt was made to prepare 6-iodo-3-aminobenzoic acid by the hydrolysis of the acetyl derivative, but the acid is very unstable, and could not be isolated. 4 : 6-*Di-iodo*-m-*toluidine*, $NH_2{\cdot}C_6H_2MeI_2$, m. p. 73—74°, crystallises in large, stout, colourless needles; the *hydrochloride* and *sulphate* were prepared; the *acetyl* derivative, m. p. 213°, forms long, slender, colourless needles, and is only slightly oxidised by potassium permanganate solution even when heated with it in a sealed tube

at 200°. 2 : 4 : 6-*Tri-iodo*-m-*toluidine*, $NH_2 \cdot C_6HMeI_3$, m. p. 135°, crystallises in long, pale brown, hair-like needles; the *acetyl* derivative has m. p. 265°. By the action of potassium iodide on the diazotisation product of 2 : 4 : 6-tri-iodo-*m*-toluidine, 2 : 3 : 4 : 6-*tetraiodotoluene*, m. p. 170°, is produced, which forms long needles.

[With Charles A. Brautlecht.]—2 : 6-*Di-iodo-aceto*-m-*toluidide*, $C_6H_2MeI_2 \cdot NHAc$, m. p. 171°, obtained by the action of iodine chloride on 2-iodoaceto-*m*-toluidide, forms colourless prisms. On hydrolysis, it is converted into 2 : 6-*di-iodo*-m-*toluidine*, m. p. 88°, which crystallises in colourless needles and prisms; the *hydrochloride* was prepared. 2 : 3 : 6-*Tri-iodotoluene*, m. p. 80·5°, prepared by the action of potassium iodide on the diazotisation product of 2 : 6-di-iodo-*m*-toluidine, forms colourless needles.

When a mixture of 6-nitro-*o*-toluidine (1 mol.) and iodine (1 mol.) with ether, water, and calcium carbonate is warmed for several hours, 5-*iodo*-6-*nitro*-o-*toluidine*, $NO_2 \cdot C_6H_2MeI \cdot NH_2$, m. p. 85°, is produced, which forms yellow prisms. By the action of potassium iodide on the diazotisation product of this base, 2 : 5-*di-iodo*-6-*nitrotoluene*,

$$NO_2 \cdot C_6H_2MeI_2,$$

m. p. 105°, is obtained, which forms colourless needles, and, on reduction, is converted into 3 : 6-*di-iodo*-o-*toluidine*, $NH_2 \cdot C_6H_2MeI_2$, m. p. 86°, which crystallises in colourless needles. On treating the diazotisation product of 3 : 6-di-iodo-*o*-toluidine with potassium iodide, 2 : 3 : 6-tri-iodotoluene is obtained in a yield of 90%. When 5-iodo-6-nitro-*o*-toluidine is diazotised in dilute sulphuric acid solution and the product is decomposed with sodium hydroxide and distilled with steam, 3-*iodo*-2-*nitrotoluene*, m. p. 65°, is obtained, which forms colourless, prismatic plates.

[With Samuel R. Scholes.]—When 4-iodo-3-nitrotoluene is reduced with ferrous sulphate and ammonia, 4-iodo-*m*-toluidine is produced, which has m. p. 38—38·5°, and not 48° as stated by Willgerodt and Simonis (Abstr., 1906, i, 156); the *phenylthiocarbamide* derivative, $C_6H_3MeI \cdot NH \cdot CS \cdot NHPh$, has m. p. 162—163°. 4-Iodoaceto-*m*-toluidide has m. p. 151°, instead of 145—146° as given by Willgerodt and Simonis (*loc. cit.*), and is converted by iodine chloride into 4 : 6-di-iodoaceto-*m*-toluidide. By the action of iodine on 4-iodo-*m*-toluidine, 4 : 6-di-iodo-*m*-toluidine is produced. 3 : 4 : 6-*Tri-iodotoluene*, m. p. 119—120°, obtained by diazotising 4 : 6-di-iodo-*m*-toluidine and treating the product with potassium iodide, forms long, slender, brown needles.

When 3-nitro-*p*-toluidine is warmed with iodine chloride and glacial acetic acid, 5-*iodo*-3-*nitro*-p-*toluidine*, m. p. 98°, is obtained, which crystallises in golden-brown needles, and yields an acetyl derivative, m. p. 202—203°, identical with that obtained by Wheeler and Liddle (this vol., i, 18) by the action of nitric acid on 3-iodoaceto-*p*-toluidide. By diazotising 5-iodo-3-nitro-*p*-toluidine and treating the product with potassium iodide, 4 : 5-*di-iodo*-3-*nitrotoluene*, m. p. 84—85°, is produced, which forms rectangular, orange prisms, and on reduction is converted into 4 : 5-*di-iodo*-m-*toluidine*, m. p. 66—67°, which forms a mass of colourless, slender needles, and yields an *acetyl* derivative, m. p. 183—184°.

5-Iodo-3-nitrotoluene, m. p. 77°, obtained by the action of potassium iodide on the diazotisation product of 5-nitro-*m*-tolnidine, forms yellow, rectangular prisms. On reduction, it is converted into *5-iodo-m-toluidine*, m. p. 78—78·5°, which crystallises in long, colourless needles; the *acetyl* derivative has m. p. 183°. E. G.

[Preparation of 5-Nitro-*m*-anisidine.] Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 222062).—*5-Nitro-m-anisidine*, $OMe\cdot C_6H_3(NH_2)\cdot NO_2$, orange-yellow needles, m. p. 120°, is prepared by the reduction of 3 : 5-dinitroanisole, m. p. 105°; the *3-nitroanisole-5-azo-β-naphthol* obtained when it is diazotised and coupled with β-naphthol can be employed for the preparation of lakes. F. M. G. M.

Condensation of Some Primary Aromatic Amines with Chloralaniline. Stroud Jordan (*J. Amer. Chem. Soc.*, 1910, **32**, 973—977).—It is well known that when an amine (1 mol.) is treated with an aldehyde (1 mol.) an additive compound is produced, whilst if the reagents are in the proportion of 2 mols. of the amine to 1 mol. of the aldehyde, a condensation product is formed and water (1 mol.) is eliminated. The experiments now described show that, in certain cases, the additive compound is an intermediate step in the formation of the condensation product, and that it can be converted into the latter on the addition of an excess of free amine.

When an alcoholic solution of freshly prepared chloralaniline is heated with aniline, the condensation product, $CCl_3\cdot CH(NHPh)_2$, is obtained.

If chloralaniline is heated with 3-nitro-*p*-toluidine dissolved in benzene, a condensation product, $CCl_3\cdot CH(NHPh)\cdot NH\cdot C_6H_3Me\cdot NO_2$, m. p. 98—99°, is obtained, which forms a yellow, crystalline mass, and is difficult to purify owing to the facility with which it decomposes with production of 5-chloro-3-nitro-*p*-toluidine. E. G.

Preparation of Optically Active *o*-Dihydroxyphenylalkylamines. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 222451. Compare this vol., i, 372).—It is found that the synthetic optically inactive racemic *o*-dihydroxyphenylalkylamines can be resolved by means of optically active tartaric acids; by this method, *l*-β-3 : 4-trihydroxyphenylethylmethylamine, identical with the therapeutically important base, *l*-adrenaline, has been obtained. Racemic β-3 : 4-trihydroxyphenylethylmethylamine (50 parts) is treated with *d*-tartaric acid (43 parts) in either aqueous or alcoholic solution, the solvent removed under reduced pressure, and the residue dried; it is then stirred with methyl alcohol in which *l*-trihydroxyphenylethylmethylamine *d*-tartrate is insoluble, this is crystallised from a mixture of methyl and ethyl alcohols (when pure it has m. p. 149°), and on treatment with alkali yields *l*-adrenaline, m. p. 211—212°. The methyl-alcoholic extract yields the more soluble *d*-trihydroxyphenylethylmethylamine. If *l*-tartaric acid is employed, the *d*-base *l*-tartrate is obtained as the most insoluble component of the mixture. Other racemic dihydroxyphenylalkylamines can be similarly resolved into their active components. F. M. G. M.

Unsymmetrical Aromatic Derivatives of Oxamide. H. Suida, jun. (*Monatsh.*, 1910, 31, 583—616).—A number of unsymmetrical disubstituted oxamides of the type of phenyltolyloxamide have been prepared by the action of arylamines on ethyl oxanilate and ethyl *p*-tolyloxamate at about 150—200°. The products, with the exception of those which contain para-substituents in both benzene nuclei, give Tafel's reaction with dichromate and concentrated sulphuric acid (Abstr., 1892, 709). The products of hydrolysis of most of the compounds have been examined (compare Dyer and Mixter, Abstr., 1887, 251). Phenyl-*p*-tolyloxamide has m. p. 204—205° (compare Heller, Abstr., 1904, i, 730). *Phenyl*-o-*tolyloxamide*,

$$NHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_4Me,$$

crystallises in microscopic prisms, m. p. 176—177°, and is rather more readily soluble than the para-compound. *Phenyl*-m-*tolyloxamide* crystallises from 60% alcohol in long, colourless, glistening needles, m. p. 168°. All three compounds when boiled with aqueous alcoholic potassium hydroxide yield a mixture of oxanilic and a tolyloxamic acid. With moderately dilute alkali and boiling for about two hours, oxalic acid does not appear to be formed.

Phenyl-p-*xylyloxamide*, $NHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_3Me_2$ [$Me_2 : NH = 1:4:2$], forms microscopic needles, m. p. 196—197°; the isomeric *meta*-compound [$Me_2 : NH = 1:3:4$] has m. p. 200—202°.

Phenyl-ψ-*cumyloxamide*, $NHPh\cdot CO\cdot CO\cdot C_6H_2Me_3$, has m. p. 202—203° when crystallised from alcohol, but 215—217° when crystallised from acetone. p-*Tolyl*-p-*xylyloxamide*, $C_6H_4Me\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_3Me_2$, crystallises from a mixture of benzene and alcohol in colourless needles, m. p. 168°. *Phenyl*-α-*naphthyloxamide*,

$$NHPh\cdot CO\cdot CO\cdot NH\cdot C_{10}H_7,$$

crystallises from alcohol in prismatic needles, m. p. 191—192°, and the isomeric β-*naphthyl* derivative forms a crystalline powder from benzene and has m. p. 227—228°. *Phenyl*-p-*nitrophenyloxamide*, $NHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2$, crystallises from ethyl acetate in yellowish-grey needles, m. p. 251—252°. *Phenyl*-o-*nitro*-p-*tolyloxamide*, $NHPh\cdot CO\cdot CO\cdot C_6H_3Me\cdot NO_2$ [$Me : NO_2 : NH = 1:3:4$], crystallises from alcohol in glistening, golden-yellow plates, m. p. 188—190°.

When phenyl-*p*-tolyloxamide is heated on the water-bath for fifteen minutes with nitric acid (D 1·4), it yields the *o*-mononitro-derivative, m. p. 182—183° and soluble in ethyl acetate, together with the 4 : 2′-*dinitro*-compound, $C_{15}H_{12}O_6N_4$, insoluble in ethyl acetate, but crystallising from chloroform in yellow, glistening needles resembling pyrites. The constitution of the two nitro-derivatives was established by an examination of the products of hydrolysis; in the case of the dinitro-compound these were oxalic acid, *p*-nitroaniline, and 3-nitro-*p*-toluidine.

Nitric acid and iodine transform phenyl-*p*-tolyloxamide into the p-*iodo*-derivative, $C_6H_4I\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_4Me$; this crystallises in microscopic prisms, which are still solid at 280°.

Most of the diarylated oxamides when hydrolysed with dilute alcoholic potassium hydroxide yield an oxamic acid and arylamine; the hydrolysis does not, as a rule, proceed to the formation of oxalic acid. In most cases both the reactions $NHR\cdot CO\cdot CO\cdot NHR' + H_2O \rightarrow$

$NHR\cdot CO\cdot CO_2H + NH_2R'$ and $NHR\cdot CO\cdot CO\cdot NHR' + H_2O \longrightarrow NH_2R + CO_2H\cdot CO\cdot NHR'$ proceed at the same time, so that the final product consists of a mixture of the two substituted oxamic acids and of the two amines. The formation of the two acids was proved by preparing and analysing a mixture of the silver salts of the two acids. In the case of the β-naphthyl, *o*-nitro-*p*-tolyl, and *p*-nitrophenyl derivatives of oxanilide, only one acid is formed, namely, oxanilic. J. J. S.

Alkylation of Aromatic Amino-acids. III. Aminomethylbenzoic Acids. Henry L. Wheeler and Charles Hoffman (*Amer. Chem. J.*, 1910, **44**, 113—126).—It has been shown in an earlier paper (this vol., i, 381) that when the salts of *o*-, *m*-, and *p*-aminobenzoic acids are treated with alkyl halides, alkylaminobenzoic acids are produced, but that certain amino-acids which have negative atoms or groups adjacent to the amino-group yield esters under these conditions. It was therefore considered of interest to ascertain whether a similar influence is exerted by substituents which are not usually regarded as having a negative character, such as the methyl group. A study has therefore been made of the ethylation of 4-amino- and 2-amino-mesitylenic acids, and it has been found that the former yields an ester, whilst the latter yields the diethylamino-acid (30 parts), the ethylamino-derivative (10 parts), and the ester (1 part). The investigation has been extended to the ethylation of 4-amino-*m*-toluic acid and 5-iodo-4-amino-*m*-toluic acid. The former gives the ethylamino-derivative (15 parts), the diethylamino-derivative (1 part), and a small quantity of another substance, probably the ester (2 parts). 5-Iodo-4-amino-*m*-toluic acid does not readily undergo alkylation; it yields the ester (15 parts) and the diethylamino-acid (4 parts). These results show that the different behaviour of amino-acids cannot be fully explained either by the theory of stereochemical interference or by the positive or negative character of the substituents.

Ethyl 4-*aminomesitylenate*, m. p. 67°, crystallises in colourless plates.

2-*Diethylaminomesitylenic acid*, m. p. 98°, forms colourless, prismatic crystals, and gives a sky-blue fluorescence in solution in light petroleum. 2-*Ethylaminomesitylenic acid*, m. p. 190° (decomp.), crystallises in large, colourless prisms.

4-Nitro-*m*-toluic acid was prepared by the nitration of *m*-toluic acid. An isomeric acid is simultaneously produced, which has been found to be 6-nitro-*m*-toluic acid. The acid obtained by Jacobsen (Abstr., 1882, 185) in this reaction, and supposed to be the 4-nitro-derivative, was doubtless a mixture, as was also the amino-product obtained on reduction. 6-*Nitro*-m-*toluamide*, m. p. 190°, forms large, transparent prisms. 4-*Ethylamino*-m-*toluic acid*, m. p. 71—72°, crystallises in large, transparent prisms, and dissolves in light petroleum to form a solution with a sky-blue fluorescence. 4-*Diethylamino*-m-*toluic acid*, m. p. 55—57°, forms long, slender needles.

5-*Iodo*-4-*amino*-m-*toluic acid*, m. p. 212° (decomp.), crystallises in square plates. The *ethyl* ester, m. p. 70—71°, forms long, colourless

prisms. 5-*Iodo*-4-*diethylamino*-m-*toluic acid*, m. p. 125—126°, forms fine, hair-like crystals. E. G.

Preparation of Carbamino-acid Esters from 6-Amino-α-naphthol-3-sulphonic Acid. Badische Anilin- & Soda-Fabrik (D.R.-P. 221967).—The carbamino-acid alkyl or alkylaryl esters of 6-amino-α-naphthol-3-sulphonic acid (J acid) of the general formula $SO_3H\cdot C_{10}H_5(OH)\cdot NH\cdot CO_2R$ (R = alkyl or alkylaryl group) can be readily prepared by slowly dropping the required alkyl chlorocarbonate into an aqueous solution of the sodium salt of the above acid at the ordinary temperature and with continual stirring.

Sodium 6-*ethylcarbamino*-α-*naphthol*-3-*sulphonate* is readily soluble in water, the *barium* salt sparingly so.

Sodium 6-*amylcarbamino*-α-*naphthol*-3-*sulphonate* is sparingly soluble in water, and the solution readily gelatinises.

Sodium 6-*benzylcarbamino*- and 6-*nitrobenzylcarbamino*-α-*naphthol*-3-*sulphonates* are sparingly soluble in water. F. M. G. M.

Acyl Derivatives of Thioamides. Motooki Matsui (*Mem. Coll. Sci. Eng. Kyōtō*, 1909—1910, 2, 241—244).—Thiobenzamide and thio-*p*-toluamide when dissolved in benzene react with acid chlorides with the formation of nitrogen-substituted compounds of the constitution $R\cdot CS\cdot N(OCR')_2$ or $R\cdot CS\cdot N\langle\begin{matrix}CO\\CO\end{matrix}\rangle R''$. The reaction takes place at the ordinary temperature, occasional cooling being necessary. The resulting compounds are stable towards hydrochloric acid, but easily decomposed by alkalis or by reducing agents, hydrogen sulphide being one of the decomposition products in both cases.

Phthalylthiobenzamide, $C_6H_5\cdot CS\cdot N:C_2O_2:C_6H_4$, crystallises from benzene in stout violet plates containing half a molecule of benzene of crystallisation. From alcohol, it crystallises in scales, and from ether in prisms, and has m. p. 126°. *Phthalylthio*-p-*toluamide*, $C_7H_7\cdot CS\cdot N:C_2O_2:C_6H_4$, forms violet scales or needles, m. p. 179°. *Succinylthio*-p-*toluamide*, $C_7H_7\cdot CS\cdot N:C_2O_2:C_2H_4$, forms violet, needle-shaped crystals, m. p. 142°. *Acetylthiobenzamide*, $Ph\cdot CS\cdot NAc_2$, forms red plates, m. p. 94—95°. *Acetylthio*-p-*toluamide*, $C_7H_7\cdot CS\cdot NAc_2$, crystallises in red plates, m. p. 121—123°. T. S. P.

Diguaiacylphosphoric Acid. Pierre Dupuis (*Bull. Soc. chim.*, 1910, [iv], 7, 846—847. Compare Abstr., 1908, i, 529; this vol., i, 248).—On adding phosphoric anhydride to guaiacol and heating to 110°, a mixture of mono- and di-guaiacylphosphoric acids is formed, from which the former may be separated by neutralisation with sodium carbonate solution and precipitation with copper sulphate. From the filtrate, diguaiacylphosphoric acid separates on adding hydrochloric acid, and can be recrystallised from boiling water. The *potassium* salt is isomorphous with the sodium salt (*loc. cit.*), and crystallises with 1 mol. H_2O. T. A. H.

Preparation of Hexa- and Penta-methylphloroglucinol. Josef Herzig and Br. Erthal (*Monatsh.*, 1910, **31**, 827—831).—The

methylation in the nucleus of phloroglucinol and orcinol (Herzig and Wenzel, Abstr., 1906, i, 93) is a complicated reaction, and the yield is dependent on factors which are still imperfectly understood.

Hexamethylphloroglucinol could not be prepared by Spitzer's method (Abstr., 1890, 1110), but both hexa- and penta-methyl derivatives are obtained on warming phloroglucinol in aqueous alkaline solution with methyl iodide until the reaction is neutral. The hexamethyl derivative crystallises out, and the pentamethyl derivative is extracted from the residue with ether. The yield is satisfactory, but the relative proportions of the two products vary in the different experiments. The pentamethyl derivative can be further methylated to hexamethylphloroglucinol by the same treatment in aqueous solution, a transformation which does not take place in alcohol.

Pentamethylphloroglucinol is converted by the action of diazomethane into the methyl ether, m. p. 52—55°, which was previously known as a viscid oil obtained by the action of methyl iodide and potassium hydroxide. E. F. A.

Some Cyclic Ethylenic Ethers and their Bromo-derivatives. G. Busignies (*Compt. rend.*, 1910, **151**, 515—517).—The Grignard reaction proceeds much more readily with substituted alkyloxy-aromatic ketones than with the alkylamino-ketones studied previously (Abstr., 1909, i, 736). Phenyl phenetidyl ketone yields in this way *phenyl*-p-*phenetidylethylene*, m. p. 71°, *phenyl*-p-*phenetidylpropylene*, m. p. 54°, and p-*phenetidylstilbene*, m. p. 93°.

The bromination of phenyl-*p*-anisylethylene has been studied, but the author has been unable to obtain the isomeric monobromo-derivatives described by Stoermer and Simon (Abstr., 1905, i, 53). Compounds of this class containing the grouping $CH_2{:}C{:}$ yield only dibromo-derivatives even in the cold, whilst those containing the grouping $\cdot CH{:}C{:}$ furnish monobromo-derivatives with liberation of hydrogen bromide. Phenyl-*p*-anisylethylene gives a *dibromo*-derivative, $C_{15}H_{14}OBr_2$, m. p. 115°; the corresponding compound from phenyl-*p*-phenetidylethylene has m. p. 90°. *β-Bromo-α-phenyl*-p-*phenetidylpropylene* has m. p. 48°. *β-Bromo-α*-p-*phenetidylstilbene*, m. p. 73°, forms a *dibromo*-derivative, $C_{22}H_{18}OBr_2$, m. p. 150°. *β-Bromodi*-p-*phenetidylpropylene* has m. p. 60°. W. O. W.

Catalytic Preparation of Mixed Ethers from Alcohols and Phenols. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1910, **151**, 359—362. Compare this vol., i, 294, 456, 536).—Phenol (1 vol.) and methyl alcohol (1·5 vols.) in the state of vapour are passed over a column of thorium oxide at 390—420°. The products are fractionated, and the middle portion washed with sodium hydroxide solution. Anisole is thus obtained in excellent yield after a single rectification. Under the same conditions, *m*-cresol gives a very good yield of the methyl ether, but with the para-compound the yield is less satisfactory. The method is successful with 2 : 4-xylenol, thymol, carvacrol, β-naphthol, and α-naphthol. In the latter case the catalyst is kept at about 400°, and the yield is 33%.

Ethers were not obtained from dihydric phenols owing to the

formation of stable compounds with the thorium oxide, these being slowly decomposed with formation of complex products.

The homologues of anisole are obtained with less ease owing to the readiness with which the higher alcohols undergo dehydration. The reaction, however, offers an advantageous means of preparation if the phenol is dissolved in excess of the alcohol. The ethyl, propyl, and *iso*amyl ethers of phenol, and *p*-tolyl ethyl ether were prepared in this way. W. O. W.

Catalytic Preparation of Phenylic and Diphenylic Ethers. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1910, **151**, 492—494. Compare preceding abstract).—Diphenyl oxide and its homologues are readily prepared by passing the vapour of a phenol over thorium oxide at 390—450°. Solid phenols may be dissolved in benzene before vaporisation. The catalytic method gives a yield of 50% of the oxide in the case of phenol and *p*- and *m*-cresol. With *o*-cresol, however, a higher temperature is necessary and the yield is poor.

When the reaction is allowed to proceed at a higher temperature, hydrogen is liberated and a diphenylene oxide produced. In the case of phenol and *p*-cresol, considerable quantities of the condensed oxides are formed at 475°; *m*-cresol under these conditions gives rise to m-*ditolylene oxide*, $C_{14}H_{14}O$, brilliant lamellæ, m. p. 182°. The analogous *ortho*-compound has m. p. 121°. W. O. W.

Scission of Phenolic Ethers by Organo-magnesium Compounds. Victor Grignard (*Compt. rend.*, 1910, **151**, 322—325. Compare Abstr., 1904, i, 494).—Organo-magnesium derivatives do not react with phenolic ethers under ordinary conditions. By adding magnesium, however, to a mixture of an alkyl bromide with anisole or phenetole in equimolecular proportions, employing benzene as the solvent, reaction occurs. Hydrolysis of the product in the usual way regenerates the phenolic ether, but if the solvent is removed and the residue gradually heated to 150—160° under 10—15 mm., only half the ether is recovered, the remainder having undergone conversion into phenol. Under the same conditions, estragole gave a 50% yield of *p*-allylphenol. In the case of safrole, fission takes place at the temperature of the water-bath, but the unstable dihydroxy-derivative cannot be isolated. A small quantity of a substance, probably 2-methoxy-5-allylphenol, is also produced.

The foregoing results are explained by supposing that an oxonium complex is first produced by addition, and that this undergoes scission, yielding the compound OPh·MgBr, and probably ethylene and a saturated hydrocarbon.

The results obtained by Schorigin by the action of alkyl derivatives of sodium with ethers may be explained in the same way (this vol., i, 547). W. O. W.

Action of Bromine in Presence of Aluminium Bromide on Phenyl Ethers. A. Bonneaud (*Bull. Soc. chim.*, 1910, [iv], **7**, 776—781).—Bodroux has shown (Abstr., 1898, i, 641) that in the case of phenols, bromine in excess in presence of aluminium bromide

(1) displaces all the hydrogen atoms in the nucleus; (2) leaves unchanged lateral chains of the type $\cdot CH_2R$, and (3) destroys lateral chains attached to the nucleus by $\vdots CH$ or $\vdots C$, replacing each of these by one atom of bromine. The author shows that the same rules hold good in the case of phenyl alkyl ethers, and that in addition these ethers undergo saponification and regenerate the corresponding phenols, except in the case of ethers containing two aromatic nuclei; thus, under these conditions, anisole, phenetole, and phenyl propyl ether all yield pentabromophenol, diphenyl ether furnishes *decabromodiphenyl ether*, colourless prisms, m. p. 293°, whilst the methyl and ethyl ethers of *o*-, *m*-, and *p*-cresols and the methyl and ethyl ethers of thymol and carvacrol all give the corresponding tetrabromocresols. The following new compounds were prepared by the action of the appropriate alkyl iodide on the potassium derivative of pentabromophenol, *pentabromoanisole*, m. p. 174°, *pentabromophenetole*, m. p. 136°, and *pentabromophenyl propyl ether*, m. p. 98°. T. A. H.

The Cholesterol Group. VIII. *iso*Cholesterol. A. Moreschi (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 53—57. Compare this vol., i, 317, and Darmstädter and Lifschütz, Abstr., 1898, i, 245).—Along with coprosterol and hippocoprosterol (Dorée and Gardner, Trans., 1908, 1625; Abstr., 1908, ii, 514), *iso*cholesterol belongs to the group of the hydrosterols. To obtain it, wool fat is repeatedly extracted with boiling alcohol, the residue is subjected to saponification, and the unsaponified portion is fused for some hours in contact with an excess of benzoic anhydride. The mixture of cholesteryl benzoate and *iso*cholesteryl benzoate obtained is purified by means of boiling alcohol, and by precipitation from ether with alcohol. The separation of the two substances can be effected by recrystallisation from a mixture of benzene and ether. iso*Cholesteryl benzoate* forms small needles, m. p. 199°, $[\alpha]_D^{16}$ +73·33°. It is saponified by alcoholic potassium hydroxide, yielding iso*cholesterol*, which crystallises in long, slender needles, m. p. 140—141°. The quantity formed in the saponification agrees with the formula $C_{26}H_{45}\cdot OBz$. The molecular weight of *iso*cholesterol (in naphthalene) was found to be 372—378°, agreeing with that required by the formula $C_{26}H_{45}\cdot OH$. The substance has $[\alpha]_D^{17}$ +59·1°. In ethereal solution in presence of platinum black, it is not acted on by hydrogen. The *formate* has m. p. 108—110°; $[\alpha]_D^{17}$ +46·47°. By the action of bromine on *iso*cholesterol, a *bromo*-derivative is obtained. R. V. S.

Nitration of Hemipinic Acid and its Esters. Rudolf Wegscheider and Alfons Klemenc (*Monatsh.*, 1910, **31**, 709—743).—On energetic nitration of α-methyl hemipinate, Wegscheider and Strauch (Abstr., 1908, i, 794) obtained methyl dinitrodimethoxybenzoate, and Wegscheider and Müller (Abstr., 1908, i, 896) prepared the same compound from methyl opianate; it is therefore regarded as a derivative of 2 : 3-dimethoxybenzoic acid, a conclusion based on the supposition that no wandering takes place of the methyl attached to the carbonyl group during nitration. This is confirmed by the behaviour of β-methyl hemipinate, which yields a derivative of protocatechuic acid.

Hemipinic acid yields on nitration nitrohemipinic acid and small quantities of 6-nitro-2 : 3-dimethoxybenzoic acid ; energetic nitration converts either of these or hemipinic acid itself directly into 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid. α-Methyl hemipinate forms the methyl ester of this acid, whereas β-methyl hemipinate forms methyl-2 : 6-dinitroveratrate. Lastly, dimethyl hemipinate forms dimethyl-5 : 6-dinitrohemipinate. In every instance on energetic nitration the esterified carboxyl group remains untouched ; the unprotected carbonyl, however, is eliminated and its position occupied by a nitro-group when the second nitro-group is introduced. Apparently, methoxyl groups have a greater influence than carboxyl groups on the position occupied by the new substituting substance.

The proof of the constitution of 6-nitro-2 : 3-dimethoxybenzoic acid depends on (1) the formation from hemipinic acid, (2) the fact that it differs from the three possible nitroveratric acids, (3) the fact that it cannot be esterified by methyl alcohol and hydrogen chloride, (4) that it is convertible into 4-nitrocatechol. The constitution of 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid is established by the fact that the isomeric methyl hemipinates give isomeric dinitro-derivatives ; the position 6 for one nitro-group is fixed by the formation of this acid from 6-nitro-2 : 3-dimethoxybenzoic acid, and the position 5 for the other nitro-group is established by the formation from nitrohemipinic acid.

Methyl 2 : 6-*dinitro*-3 : 4-*dimethoxybenzoate*, prepared by nitration of β-methyl hemipinate with fuming nitric acid without a solvent, crystallises in colourless, lustrous, long needles, m. p. 136—136·5°.

2 : 6-*Dinitro*isovanillic *acid*, prepared by boiling the above compound with dilute potassium hydroxide, separates in well formed crystals, m. p. 206° (decomp.). It gives a brownish-red precipitate with ferric chloride. Crystallographic measurements prove its identity with the acid described by Matthiessen and Foster (*Jahresber.*, 1867, 520) as dinitromethylhypogallic acid. It cannot be esterified by methyl alcohol and hydrogen chloride. The *silver* salt was obtained as a yellow, crystalline, explosive substance ; the *disilver* salt is red. The *methyl* ester, prepared by the interaction of methyl iodide and the mono-silver salt, crystallises in long, yellow needles, m. p. 163—164°. The *acetate* forms lustrous plates, m. p. 126—129°.

2 : 6-*Dinitroacetyl*isovanillic *acid*, prepared by heating the acid with acetic anhydride, forms a colourless, crystalline mass, m. p. 156° (decomp.).

2 : 6-*Dinitroveratric acid*, prepared by hydrolysis of the methyl ester with the calculated amount of aqueous potassium hydroxide crystallises in long, yellow needles, which soften at 191°, m. p. 194—195°. It cannot be acetylated.

Dimethyl 6-nitrohemipinate, prepared by the action of fuming nitric acid on dimethyl hemipinate, has m. p. 83—84° [Wegscheider and Rušnov (Abstr., 1908, i, 793) found 77—78°]. It crystallises in the triclinic system, $a : b : c = 1 : 0{\cdot}7192 : 0{\cdot}6303$. $\alpha = 88°0'$, $\beta = 88°56'$, $\gamma = 98°31'$.

Dimethyl dinitrohemipinate crystallises in slender, colourless needles, m. p. 120—121°. On hydrolysis, *dinitrohemipinic acid*, a colourless,

crystalline powder, m. p. 163° (decomp.), is obtained. When heated in a stream of carbon dioxide at the melting point, it is converted into the *anhydride*, m. p. 113—114°.

6-Nitro-2 : 3-dimethoxybenzoic acid (Wegscheider and Rušnov, *loc. cit.*) is colourless, m. p. 189—190°, and differs from the three known nitroveratric acids. The *methyl* ester has m. p. 76—77°. By the action of aniline, 5-nitroguaiacol is formed, which yields 4-nitroveratrole on methylation.

4-*Nitroguaiacyl acetate*, prepared from nitroguaiacol and acetic anhydride, forms colourless needles, m. p. 108—109°. E. F. A.

Two Aromatic Acids of the Series, $C_nH_{2n-8}O_2$. F. Bodroux (*Bull. Soc. chim.*, 1910, [iv], 7, 847—848).—*α-Phenyl-α-ethylbutyric acid* $CEt_2Ph\cdot CO_2H$, obtained with the amide by the hydrolysis of the corresponding nitrile (this vol, i, 482, 557), crystallises from alcohol in small, colourless prisms, m. p. 93°. *α-Phenyl-γ-methyl-α-isobutylvaleric acid*, $C(CH_2Pr^{\beta})_2Ph\cdot CO_2H$, similarly obtained (this vol., i, 482), crystallises from light petroleum in large, colourless prisms, m. p. 75—76°. T. A. H.

Synthetic Preparation of Esters of αβ-Diphenylsuccinic Acid. Telemachos Komnenos (*Annalen*, 1910, 375, 254—259).—The reaction between ethereal iodine and an alcoholic solution of ethyl phenylacetate and sodium ethoxide yields ethyl (*b*)-*αβ*-diphenylsuccinate, m. p. 140° ; the acid, m. p. 160°, obtained by its hydrolysis is probably a mixture of the *a* and *b* forms of *αβ*-diphenylsuccinic acid. Ethereal iodine reacts with a methyl-alcoholic solution of ethyl phenylacetate and sodium methoxide to form *methyl* (*a*)-*αβ-diphenylsuccinate*, $[CO_2Me\cdot CHPh]_2$, m. p. 210° ; the acid obtained by its hydrolysis softens at 187°, melts at 222° (decomp.), and forms a barium salt containing $2H_2O$, and is, therefore, (*a*)-*αβ*-diphenylsuccinic acid. C. S.

Action of Unsaturated Dicarboxylic Acids on *p*-Aminophenols. Arnaldo Piutti (*Gazzetta*, 1910, 40, i, 525—568. Compare Abstr., 1908, i, 783 ; this vol., i, 22, 264).—[With A. Pagniello and A. Marciano.]—*Citraconic Derivatives.*—p-*Hydroxyphenylcitraconamic acid*, $C_{11}H_{11}O_4N$, forms yellow, acicular prisms, m. p. 155°. p-*Methoxyphenylcitraconamic acid*, $C_{12}H_{13}O_4N$, may be obtained by the method previously given, and also (1) by saponifying *p*-methoxyphenylcitraconimide with alcoholic potassium hydroxide ; (2) by acting on *p*-anisidine (in light petroleum) with mesaconyl chloride. It crystallises in long, yellow prisms, m. p. 167°, and gives a violet coloration with ferric chloride. p-*Ethoxyphenylcitraconamic acid*, $C_{13}H_{15}O_4N$, prepared by the above methods, forms yellow needles, m. p. 162°, and gives a yellow coloration with ferric chloride.

p-*Hydroxyphenylcitraconimide*, $C_{11}H_9O_3N$, is a dark yellow, crystalline substance, m. p. 170°. p-*Methoxyphenylcitraconimide*, $C_{12}H_{11}O_3N$, forms yellow crystals, m. p. 121° ; it gives a violet coloration with alcoholic potassium hydroxide. p-*Ethoxyphenylcitraconimide*, $C_{13}H_{13}O_3N$, crystallises in canary-yellow needles, m. p. 109°.

The diamides obtained from citraconic anhydride or citraconyl chloride by the methods already indicated are found to be mesaconic derivatives, identical with those obtained directly from mesaconic acid. The *p*-hydroxyphenyl derivative could not be obtained. p-*Methoxyphenylmesacondiamide*, $C_{19}H_{20}O_4N_2$, forms colourless, lustrous scales, m. p. 206°. p-*Ethoxyphenylmesacondiamide*, $C_{21}H_{24}O_4N_2$, crystallises similarly, and has m. p. 205°.

[With C. Schifani.]—*Mesaconic Derivatives.*—Mesaconamic acids and mesaconimides could not be prepared, but in their stead corresponding citraconic derivatives appeared. On the other hand, *p*-methoxy- and *p*-ethoxy-phenylmesacondiamides were obtained, identical with those from citraconic acid (*v.s.*).

By the action of mesaconyl chloride on *p*-anisidine in addition to *p*-methoxyphenylcitraconamic acid, a colourless *substance*, m. p. 235°, was obtained.

[With Ida Foa and L. Rossi.]—*Itaconic Derivatives.*—Of the four isomeric p-*hydroxyphenylitaconamic acids*, $C_{11}H_{11}ON_4$, which might be expected, only three could be prepared. On mixing equimolecular quantities of itaconic anhydride and *p*-aminophenol, dissolved in benzene and in acetone respectively, one isomeride is precipitated; it forms colourless needles, m. p. 161—162° (forming a yellowish-brown liquid), and gives no coloration with ferric chloride. The *silver* salt was prepared. Another isomeride, a yellow, crystalline powder, m. p. 118—119°, is obtained by dissolving the corresponding imide in sodium hydroxide and precipitating with acid; it gives a red coloration with ferric chloride. When it is boiled with water, it yields the third isomeride, which is colourless, has m. p. 97—98°, and gives no coloration with ferric chloride. By similar methods, three corresponding isomeric p-*methoxyphenylitaconamic acids*, $C_{12}H_{13}O_4N$, are obtained. The first forms colourless, acicular crystals, m. p. 166—167° (forming a yellow liquid), and gives no coloration with ferric chloride. The *silver* salt was obtained. The second isomeride is yellow, and has m. p. 144—145°; it yields a red coloration with ferric chloride. The *silver* salt was prepared. The other isomeride is colourless, has m. p. 135—136°, and gives no coloration with ferric chloride. The *silver* salt was prepared. There are three corresponding isomeric p-*ethoxyphenylitaconamic acids*, $C_{13}H_{15}O_4N$. The first forms colourless, lustrous scales, m. p. 165—166°, and gives no reaction with ferric chloride. The *silver* salt was prepared. A second isomeride forms a yellow precipitate, m. p. 148—149°, and gives a red coloration with ferric chloride. The *silver* salt was prepared. The third isomeride is a colourless, crystalline substance, m. p. 134—135°. The *silver* salt was also obtained.

The imides corresponding with the above acids were prepared (1) by heating the acids in an atmosphere of carbon dioxide at a temperature a little above their melting points; (2) by heating at 130° in carbon dioxide mixtures of itaconic anhydride with the aminophenols. p-*Hydroxyphenylitaconimide*, $C_{11}H_9O_3N$, forms yellow crystals, m. p. 104—105°. p-*Methoxyphenylitaconimide*, $C_{12}H_{11}O_3N$, crystallises in small, yellow needles, m. p. 101—102°; it gives an intense, reddish-violet coloration with sodium ethoxide. p-*Ethoxyphenylitaconimide*,

$C_{13}H_{13}O_3N$, forms yellow needles, m. p. 99—100°, and gives a reddish-violet coloration with potassium or sodium hydroxide.

The itacondiamides were obtained by the method previously described. p-*Hydroxyphenylitacondiamide*, $C_{17}H_{16}O_4N_2$, crystallises in small, light brown laminæ, m. p. 132—133°. p-*Methoxyphenylitacondiamide*, $C_{19}H_{20}O_4N_2$, forms lustrous scales, m. p. 155—156° p-*Ethoxyphenylitacondiamide*, $C_{21}H_{24}O_4N_2$, crystallises similarly, and has m. p. 173—174°.

[With Gino Abati.]—*Pyrocinchonic Derivatives.*—Of the derivatives of this acid, only the imides could be prepared, in addition to *p*-anisidine *p*-methoxyphenylpyrocinchonamate,

$$C_2Me_2(CO\cdot NH\cdot C_6H_4OR)_2,$$

and *p*-phenetidine *p*-ethoxyphenylpyrocinchonamate.

p-*Hydroxyphenylpyrocinchonimide*, $C_{12}H_{11}O_3N$, was obtained by (1) heating to boiling point an alcoholic solution of pyrocinchonic anhydride and *p*-aminophenol, a current of sulphur dioxide being afterwards passed to reduce the coloration of the liquid; (2) mixing the two substances in the presence of acetone in the cold, sulphur dioxide being afterwards employed to decolorise the liquid. In the latter case, indications were obtained of the formation and subsequent decomposition of *p*-aminophenol *p*-hydroxyphenylpyrocinchonamate. When the imide is treated with alcoholic potassium hydroxide and then acidified, it separates out unchanged. The imide forms large, canary-yellow crystals, m. p. 200°. When it is precipitated from alcohol with water, or when it is powdered in a mortar, it is obtained in colourless crystals, which have the same m. p. and composition as the other form.

p-Anisidine and pyrocinchonic anhydride in alcoholic solution in the warm, and in acetone at the ordinary temperature, yield p-*methoxyphenylpyrocinchonimide*, $C_{13}H_{13}O_3N$, crystallising in straw-yellow prisms, m. p. 139°. From some solvents it is obtained in colourless crystals, which become yellow on melting, and remain so on resolidification. *p*-Anisidine and the anhydride react in benzene solution at the ordinary temperature, yielding p-*anisidine* p-*methoxyphenylpyrocinchonamate*, $C_{20}H_{24}O_5N_2$, which forms small, white needles, m. p. 90—91° (becoming yellow at about 85°). In solution (in ethylene bromide) the substance decomposes into its three constituents. p-*Ethoxyphenylpyrocinchonimide*, $C_{14}H_{15}O_3N$, forms lustrous, yellow needles, m. p. 117°. The colourless form has m. p. 116—117°. p-*Phenetidine* p-*ethoxyphenylpyrocinchonamate* crystallises in minute, colourless needles, which become yellow at 80° and melt at 94° to a yellow liquid, which remains yellow on solidification.

[With C. Allegri.]—*Phthalic, Citraconic, Itaconic, and Maleic Derivatives of* o-*Anisidine.*—o-*Methoxyphenylphthalamic acid*,

$$C_{15}H_{13}O_4N,$$

forms colourless crystals, m. p. 168—169°, and gives with ferric chloride a yellow coloration, which becomes reddish-violet. o-*Methoxyphenylcitraconamic acid*, $C_{12}H_{13}O_4N$, crystallises in canary-yellow needles, m. p. 116—117°, and yields an intense reddish-violet coloration with ferric chloride. o-*Methoxyphenylitaconamic acid*, $C_{12}H_3O_4N$, forms small, colourless needles, m. p. 128—129°, and gives a pale

violet coloration with ferric chloride. o-*Methoxyphenylmaleinamic acid*, $C_{11}H_{11}O_4N$, an amorphous, yellow powder, has m. p. 144—145°, and gives with ferric chloride a wine-red coloration.

o-*Methoxyphenylphthalimide*, $C_{15}H_{11}O_3N$, crystallises in colourless prisms, m. p. 155—156°. o-*Methoxyphenylcitraconimide*, $C_{12}H_{11}O_3N$, a pale yellow powder, has m. p. 98—99°, and gives a violet coloration with alcoholic potassium hydroxide. o-*Methoxyphenylitaconimide*, $C_{12}H_{11}O_3N$, is a colourless powder, m. p. 112—113°. *o*-Methoxyphenylmaleinimide could not be obtained.

[With G. Leone and C. D'Emilio.]—*Camphoric Derivatives.*—α-cis-p-*Hydroxyphenylcamphoramic acid*, $\begin{matrix}H\\Me\end{matrix}\!>\!C_7H_{10}\!<\!\begin{matrix}CO\cdot NH\cdot C_6H_4\cdot OH\\CO_2H\end{matrix}$, prepared by heating camphoric anhydride and *p*-aminophenol in boiling acetone for half an hour, has m. p. 165° (becoming brown at 155°), $[\alpha]_D^{16}$ +46·36°. α-trans-p-*Hydroxyphenylcamphoramic acid*, $\begin{matrix}H\\CO_2H\end{matrix}\!>\!C_7H_{10}\!<\!\begin{matrix}CO\cdot NH\cdot C_6H_4\cdot OH\\Me\end{matrix}$, is obtained when an aqueous solution of the potassium salt of the preceding acid is heated for ten hours in an autoclave at 120°, and then treated with hydrochloric acid; it has m. p. 226°, $[\alpha]_D^{16}$ +13·48°. α-p-*Hydroxyphenylcamphoramic acid* (?), $C_{16}H_{21}O_4N$, from camphoric anhydride and *p*-aminophenol in acetone at the ordinary temperature, becomes brown at 205° and decomposes at 220°, and has $[\alpha]_D^{16}$ +52·4°. When heated in alcoholic solution, it is converted into the *α-cis*-form, m. p. 165°. A p-*hydroxyphenylcamphoramic acid* (?), $C_{16}H_{21}O_4N$, is also obtained by heating camphoric anhydride and *p*-aminophenol in a sealed tube for five hours at 210°. It forms colourless crystals, m. p. 185°, $[\alpha]_D^{16}$ +12·4°. A p-*methoxyphenylcamphoramic acid* (?), $C_{17}H_{23}O_4N$, is obtained on mixing benzene solutions of camphoric anhydride and *p*-anisidine. It forms large, colourless prisms, m. p. 198°. α-cis-p-*Ethoxyphenylcamphoramic acid*, $C_{18}H_{25}O_4N$, is prepared by heating camphoric anhydride with *p*-phenetidine for two hours, or by heating without a solvent for eight hours in an autoclave. It forms colourless crystals, m. p. 199°, $[\alpha]_D^{16}$ +51·4°. α-trans-p-*Ethoxyphenylcamphoramic acid* is obtained in the same way as the corresponding methoxy-derivative. It has m. p. 184°, $[\alpha]_D^{25}$ +2·81°.

p-*Hydroxyphenylcamphorimide*, $C_{16}H_{19}O_4N$ (from camphoryl chloride and *p*-aminophenol in acetone), has m. p. 218°, $[\alpha]_D^{25}$ +5·49°. p-*Methoxyphenylcamphorimide*, $C_{17}H_{21}O_3N$, forms colourless crystals, m. p. 110°. p-*Ethoxyphenylcamphorimide* crystallises in colourless needles, m. p. 114°, $[\alpha]_D^{25}$ −13·28°.

[With D. Pugliese and G. Selvaggi.]—iso*Phthalic and Terephthalic Derivatives.*—No product of the action of *iso*phthalic acid on *p*-aminophenol in boiling alcohol could be isolated. The reactions with *p*-anisidine and *p*-phenetidine respectively, under the same conditions, yielded p-*anisidine hydrogen phthalate*, which on heating becomes brown above 200°, and p-*phenetidine hydrogen phthalate*, which becomes brown on heating above 100°. p-*Methoxyphenyl*iso*phthaldiamide*, $C_6H_4(CO\cdot NH\cdot C_6H_4\cdot OMe)_2$, was obtained, however, by heating the acid with *p*-anisidine to 280°.

It crystallises in colourless needles, m. p. 268°. p-*Methoxyphenylterephthaldiamide*, similarly obtained by heating to 150°, forms lustrous scales, m. p. 246—248°. p-*Ethoxyphenylterephthaldiamide*, similarly prepared by heating at 180° for two hours, forms grey needles, which, on heating to 300°, become brown, but do not melt. R. V. S.

Galloflavin. VI. Lactone Dyes. Josef Herzig [with Geza Erdös and Grete Ruzicka] (*Monatsh.*, 1910, 31, 799—818. Compare Herzig and Epstein, Abstr., 1908, i, 899).—Galloflavin belongs to quite a different class of substances than resoflavin, which is classed as a derivative of diphenylbimethylolide. Galloflavin is completely methylated by diazomethane (Herzig and Tscherne, Abstr., 1904, i, 814). Unlike resoflavin, on further treatment of this methylated derivative with potassium hydroxide and methyl sulphate or methyl iodide, it cannot be converted into the methyl ethyl ester, but yields a mixture of tarry products. A further point of difference is in the behaviour towards potassium hydroxide; methyl galloflavin dissolved in the cold yields on acidification a hydrolysed substance with fewer methoxyl groups, and the latter when methylated gives a substance isomeric with the original. The new compound is provisionally termed iso*galloflavin trimethyl ether*, $C_{12}H_3O_5(OMe)_3$, and the new ether is iso*galloflavin tetramethyl ether*, $C_{12}H_2O_4(OMe)_4$. Galloflavin, therefore, has the formula $C_{12}H_2O_4(OH)_4$, with which the analysis of the acetyl derivative agrees.

The conversion into *iso*galloflavin trimethyl ether gives only about 45% of the theoretical yield, together with a syrupy product.

*iso*Galloflavin trimethyl ether is a pronounced acid; at the melting point carbon dioxide is eliminated, forming the *compound*,

$$C_{11}H_3O_3(OMe)_3.$$

It contains a lactone ring which is opened by treatment with potassium hydroxide and methyl iodide or sulphate, yielding a crystalline substance. This *ether* ester is quantitatively hydrolysed to the *ether acid*, $C_{10}H_2O(OMe)_4(CO_2H)_2$, which again loses carbon dioxide at the melting point, forming an acid, $C_{10}H_3O(OMe)_4{\cdot}CO_2H$. It remains to determine the function of the last oxygen atom, the constitution of the complex, $C_{10}H_8$ or $C_{10}H_{10}$, and the relation of the *iso*-derivative to galloflavin.

Purpurogallin, $C_{11}H_4O(OH)_4$, has been shown by A. G. Perkin to undergo an isomerisation with potassium hydroxide similar to galloflavin, and it is possible that the C_{10} complex is the same in each case.

Tetra-acetylgalloflavin is colourless, m. p. 230—233°. Galloflavin tetramethyl ether forms colourless, matted needles, m. p. 236—239°. iso*Galloflavin trimethyl ether* forms colourless needles, m. p. 253—256° (decomp.). iso*Galloflavin tetramethyl ether* crystallises in well-formed, long needles, m. p. 232—234°, mixed m. p. with the isomeride 205—211°.

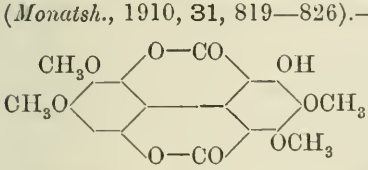
The *compound*, $C_{11}H_3O_3(OMe)_3$, formed on heating *iso*galloflavin trimethyl ether, separates from alcohol in colourless crystals, m. p. 130—134°.

The *ether* ester, $C_{12}H_2O_3(OMe)_6$, has m. p. 93—95°; the *ether acid*, $C_{12}H_4O_5(OMe)_4$, is colourless; it becomes coloured at 205°, m. p.

214—215° (decomp.). Heated at 210—220°, carbon dioxide is eliminated, and the *compound*, $C_{11}H_4O_3(OMe)_4$, m. p. 132—134°, is obtained.

Acetylpurpurogallin forms colourless plates, m. p. 181—183°. Tetramethylpurpurogallin is colourless, m. p. 91—92° (compare Perkin, Proc., 1905, 21, 211). E. F. A.

Condensation Products of Gallic Acid Di- and Tri-methyl Ether. VII. Lactone Dyes. Josef Herzig and F. Schmidinger (*Monatsh.*, 1910, 31, 819—826).—By the condensation of either gallic acid 3 : 4-dimethyl ether or gallic acid trimethyl ether by means of potassium persulphate, *flavellagic acid tetramethyl ether* (annexed formula), a yellow dye, is obtained.



When purified through the *acetyl* derivative, m. p. 237—238°, it crystallises in minute, sulphur-yellow needles, m. p. 270—271°.

By the action of potassium hydroxide and methyl sulphate, the lactone ring is opened, and flavellagic acid methyl ether ester (the completely methylated product), m. p. 81°, is obtained (compare Herzig and Tscherne, Abstr., 1908, i, 547). Diazomethane is entirely without action on the condensation product, although this readily converts flavellagic acid into the pentamethyl derivative. Apparently the resistant hydroxyl is rendered so by the presence of the methoxyl groups, and the same group is methylated at an early stage in the case of flavellagic acid itself. E. F. A.

Synthesis of Glucosyringic Acid. Ferdinand Mauthner (*J. pr. Chem.*, 1910, [ii], 82, 271—274).—*Methyl tetra-acetylglucosyringate*, $C_{24}H_{30}O_{14}$, m. p. 106—107°, obtained by shaking a solution of methyl syringate in aqueous sodium hydroxide with ethereal β-acetobromoglucose for twenty-four hours, is hydrolysed by 6% barium hydroxide, whereby is obtained glucosyringic acid identical with that produced by the oxidation of syringin. C. S.

Degradation of *cyclo*Gallipharic Acid by Oxidising Agents. Hermann Kunz-Krause and Paul Manicke (*Arch. Pharm.*, 1910, 248, 398—420).—When *cyclo*gallipharic acid, hydrolysed by sodium hydroxide, is heated for twelve hours on the water-bath with the gradual addition of 3·5% hydrogen peroxide, carbon dioxide and acraldehyde are evolved, and, after acidification, a colourless, crystalline monobasic *acid*, $C_{18}H_{34}O_3$, m. p. 76°, is obtained, which develops a bluish-violet coloration with alcoholic ferric chloride. This reaction suggests that the acid is still a cyclic compound containing hydroxyl and carboxyl groups in the ortho-position; the acid is an oxidation product intermediate between *cyclo*gallipharic acid and gallipharic acid, and consequently is called cyclomeso*gallipharic acid*. When *cyclo*gallipharic acid and an excess of sodium hydroxide on the water-bath are treated with 3·5% hydrogen peroxide until the bluish-violet coloration is no longer produced with ferric chloride, the products of

oxidation are found to be acraldehyde, butyric acid, and gallipharic acid, m. p. 57·5° (not 54°).

The oxidation of *cyclo*gallipharic acid by sodium carbonate and 3% potassium permanganate has been shown to produce butyric and oxalic acids, glycerol, and gallipharic acid, m. p. 54° (Kunz-Krause and Schelle, Abstr., 1904, i, 587). The gallipharic acid is now shown, by analyses of the acid and of the sodium and silver salts, to be a mixture of about 75% gallipharic acid, m. p. 57·5°, and 25% of *gallipinic acid*, $C_{14}H_{28}O_2$, m. p. 49°, which is separable by dilute alcohol. In addition to these two, a small quantity of a third acid, *polycyclopharic acid*, $C_{30}H_{60}O_5$, m. p. 35°, has been isolated, which gives a Bordeaux-red coloration with ferric chloride, and develops in the liquid state an olive-green fluorescence and a pronounced odour of oranges. The greater part of these acids is absorbed by the hydrated manganese dioxide produced during the oxidation, and is extracted therefrom, after drying, by alcohol. The residue is freed from manganese dioxide by hot concentrated oxalic acid, and the residual yellow mass is purified by repeated solution in acetone and evaporation of the solvent, whereby a reddish-brown resin, *resocyclopharol*, $C_{15}H_{24}O_3$, m. p. 93°, is obtained, which has a pleasant odour of oranges, and in solution an acid reaction and olive-green fluorescence.

The oxidation of *cyclo*gallipharic acid by alkaline potassium permanganate yields 28·10% of gallipinic and gallipharic acids, 44·96% of resocyclopharol, 16·20% of oxalic acid, 1·64% of butyric acid, and 2·20% of glycerol. C. S.

Anthraquinone-2 : 3-dicarboxylic Anhydride. Conrad Willgerodt and Francesco Maffezzoli (*J. pr. Chem.*, 1910, [ii], 82, 205—231).—The following results are the outcome of an unsuccessful attempt to obtain an anthraquinone-indigotin from anthraquinone-2 : 3-dicarboxylic anhydride by a method analogous to Heumann's synthesis.

Anthraquinone-2 : 3-dicarboxylic anhydride, which is precipitated almost quantitatively when the acid is boiled with acetic anhydride for fifteen minutes, is best converted into the imide by heating its intimate mixture with ammonium thiocyanate at 160—170° for five minutes, or with carbamide at 175—180° for one hour. *Anthraquinone-3-carbonamide-2-carboxylic acid*, $C_6H_4<^{CO}_{CO}>C_6H_2(CO\cdot NH_2)\cdot CO_2H$, m. p. above 340°, prepared by dissolving the imide in dilute alkali at 40—50°, is converted into 3-*aminoanthraquinone-2-carboxylic acid*,

$$C_6H_4<^{CO}_{CO}>C_6H_2(NH_2)\cdot CO_2H,$$

by oxidising its alkaline solution with freshly prepared sodium hypobromite, or, better, with 5·4% sodium hypochlorite, at 80—85°, or, quantitatively, with iodosobenzene; in all three cases a blood-red, crystalline alkali salt is precipitated, from which the amino-acid is liberated by hydrochloric acid and recrystallised from nitrobenzene; it then separates in orange-yellow needles. The amino-acid, the *ammonium*, *sodium*, *silver*, and *barium* salts of which are described, does not yield salts with acids, forms a yellow *acetyl*

derivative, m. p. 248°, yields 2-aminoanthraquinone by the heating of its silver salt, and is converted into anthraquinone-2-carboxylic acid when the amino-group is replaced by hydrogen in the usual way. When heated with chloroacetic acid for half an hour, it yields, not the desired glycine derivative, but *3-chloroacetylaminoanthraquinone-2-carboxylic acid*, $C_6H_4<^{CO}_{CO}>C_6H_2(CO_2H)\cdot NH\cdot CO\cdot CH_2Cl$, m. p. 350°, which forms microscopic, orange crystals. When a pyridine solution of the imide mentioned above is diluted with an equal volume of alcohol and treated with alcoholic potassium hydroxide, the *potassium* derivative, $C_6H_4<^{CO}_{CO}>C_6H_2<^{CO}_{CO}>NK$, is obtained as a brownish-grey powder, which is converted by water at 40—50° into potassium anthraquinone-3-carbonamide-2-carboxylate, and reacts with ethyl chloroacetate at 150—160° to form the *ester*,

$$C_6H_4<^{CO}_{CO}>C_6H_2<^{CO}_{CO}>N\cdot CH_2\cdot CO_2Et,$$

m. p. 241—242°. When treated with the calculated quantity of sodium hydroxide solution at 40—50°, this ester yields the *compound*, $C_6H_4<^{CO}_{CO}>C_6H_2(CO_2H)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 313—314°, an alkaline solution of which is converted by sodium hypochlorite into anthraquinone-2-carboxylic acid, anthraquinone-2 : 3-dicarboxylic acid, and 3-aminoanthraquinone-2-carboxylic acid.

Anthraquinonefluorescein,

$$C_6H_4<^{CO}_{CO}>C_6H_2<^{CO\cdot O}_{\quad\quad\quad}>C<^{C_6H_3(OH)}_{C_6H_3(OH)}>O,$$

which is obtained by adding zinc chloride to an intimate mixture of resorcinol and anthraquinone-2 : 3-dicarboxylic anhydride at 150° and heating the mass at 180—190° for five to six hours (the purification of the product is troublesome), crystallises in yellow needles, m. p. above 380°. It forms in concentrated alkali a dark cherry-red, non-fluorescent solution, which becomes reddish-yellow by dilution and then exhibits a very feeble red fluorescence. The *ammonium*, *silver*, *barium*, *calcium*, *magnesium*, and *lead* salts of the fluorescein, which possesses feeble acid properties, are described. The *diacetyl* derivative, m. p. 259—260°, is hydrolysed by boiling alcoholic alkalis or by cold concentrated sulphuric acid, but not by boiling concentrated hydrochloric acid. When the powdered fluorescein is exposed in a desiccator to bromine vapour for three to four hours, it is converted into a red *dibromoanthraquinonefluorescein*, $C_{28}H_{12}O_7Br_2$, m. p. 313° (decomp.), which is soluble in alkalis and forms highly coloured salts. *Tetrabromoanthraquinonefluorescein*, $C_{28}H_{10}O_7Br_4$, m. p. 367° (decomp.), is obtained by adding the calculated amount of bromine to a cold alcoholic solution of anthraquinonefluorescein and precipitating the substance by water. The alkali salts of this and of the dibromo-derivative are dyes which have a great affinity for animal fibres.

Anthraquinone-2 : 3-dicarboxylic anhydride, quinaldine, and zinc chloride react at 180—190° to form a *substance*,

$$C_6H_4<^{CO}_{CO}>C_6H_2<^{CO\cdot O}_{\quad\quad\quad}>C:CH\cdot C_9NH_6,$$

which crystallises in microscopic, yellow needles, does not melt below 380°, and dissolves unchanged in concentrated sulphuric acid.

C. S.

Piperonylidene Diacetate. Jan J. Blanksma (*Chem. Weekblad*, 1910, 7, 713—715).—Acetic anhydride in the presence of a drop of sulphuric acid converted piperonal into *piperonylidene diacetate*, which separated from alcohol in colourless, transparent crystals, m. p. 51°. After a time these crystals became opaque, their m. p. having changed to 80°. Various attempts to obtain again the modification with m. p. 51° were made, but proved unsuccessful. A. J. W.

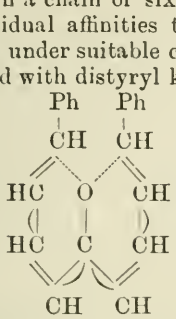
Synthesis of a New Gallacetophenone Trimethyl Ether. Ferdinand Mauthner (*J. pr. Chem.*, 1910, [ii], 275—280).—3 : 4 : 5-*Trimethoxyphenyl methyl ketone*, $CH_3 \cdot CO \cdot C_6H_2(OMe)_3$, m. p. 72°, is obtained by the action for fourteen days of ethereal diazomethane on a benzene solution of gallaldehyde trimethyl ether. A more convenient process starts from ethyl 3 : 4 : 5-trimethoxybenzoylacetate (best prepared by the condensation of ethyl acetate and methyl gallate trimethyl ether under the influence of sodium), which is converted into the ketone by heating for nine hours with 25% sulphuric acid. The p-*nitrophenylhydrazone*, m. p. 195—196°, separates from hot alcohol in reddish-brown needles; the *semicarbazone* has m. p. 178—179°.

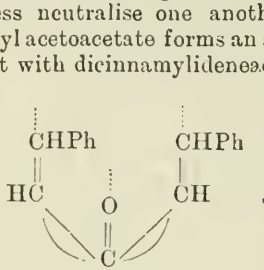
C. S.

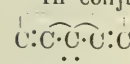
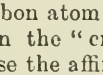
Distribution of Affinity in Unsaturated Organic Compounds. Walther Borsche (*Annalen*, 1910, 375, 145—180).—In a conjugated system of two unsaturated groups, the residual affinities of the inner pair of unsaturated atoms neutralise each other, leaving free residual affinity only at the two external unsaturated atoms, where addition takes place. Thiele's conception, thus stated, is incorrect, for the inner pair of atoms still retain the power of increasing the mobility of univalent atoms attached to them through the intermediary of saturated multivalent atoms, and therefore still retain residual affinity. (According to Thiele, the increased mobility of a univalent atom, exhibited when the atom is attached to an unsaturated group through the intermediary of a saturated multivalent atom, as, for example, $\cdots C{:}O \cdots$ / $\dot{O}H$, is caused by the influence of the residual affinity of the unsaturated carbon atom on the hydroxylic oxygen atom, whereby the hold of the latter on the hydrogen is weakened.) The affinity (strictly speaking, that portion of the affinity which denotes the unsaturation) of an unsaturated atom in a conjugated system, therefore, is divided into three parts; for example, in the system, $\overset{\alpha}{C}{:}\overset{\beta}{C}\cdot\overset{\gamma}{C}{:}\overset{\delta}{C}$, the affinity of C_β is divided into (i) the portion denoted in the double linking, (ii) the portion which is neutralised by the corresponding portion of the affinity of C_γ, (iii) the portion which persists as free residual affinity. At present little can be stated with regard to the quantitative proportions of these three parts; most probably they are different in each individual case. The distribution of the affinity in a conjugated system of

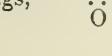
two unsaturated groups is such that there is a tendency for the neutralisation of the residual affinities of the inner pair of unsaturated atoms, and for the accumulation of residual affinity at the outer pair.

The distribution of the affinity in a conjugated system of three unsaturated groups forming a straight chain is very similar to the preceding, but the accumulation of residual affinity at the outer unsaturated atoms does not necessarily indicate great additive capacity, because in a chain of six atoms the last is near enough to the first for their residual affinities to more or less neutralise one another; for example, under suitable conditions, ethyl acetoacetate forms an additive compound with distyryl ketone, but not with dicinnamylideneacetone:





In conjugated systems containing "crossed" doubling linkings,  , there are three outer atoms at which the residual affinity can collect, and therefore the distribution of the affinity is more complicated. In the simple system  , the affinity of the carbonyl carbon atom neutralises more or less that of the adjacent carbon atom; in the "crossed" system the central carbon atom, in order to neutralise the affinities of each of the adjacent carbon atoms, utilises more of its affinity; consequently, the oxygen atom has a greater amount of free residual affinity. There is more residual affinity at the three outer unsaturated atoms in a conjugated system of crossed double linkings than at the ends of a chain of three unsaturated groups forming a conjugated system; in the former system the neutralisation of the affinities of the three inner unsaturated atoms is less complete, the state of equilibrium first attained is more labile, and the system is more prone to enter into reaction. Such reactions will occur preferentially at the oxygen atom (or other multivalent atom attached to the central carbon atom), the more so as the unsaturated atoms at the other two ends of the crossed system are so situated as to neutralise each other's residual affinity more or less completely.

The views developed above have been tested by experiments on the addition of ethyl acetoacetate and other compounds containing activated methylene groups to $\alpha\beta$-unsaturated ketones of the type of distyryl ketone, therefore, to substances containing the conjugated system of crossed double linkings,  .

According to the old view, a carbonyl group increases the additive power of a contiguous ethylenic linking without itself playing an active part in the addition. Consequently, there should be less tendency for the addition of a molecule, XY, to substances containing such a system than to substances containing the group $\overset{\cdot\cdot}{\underset{O}{C:C\cdot C\cdot}}$, because in the former case the activating influence of the carbonyl group is diffused over two ethylenic linkings. When, however, one molecule of XY has been attached, the resulting system, CX·CY·CO·C:C, will have a greater additive power than the original system; consequently, the final product should be CX·CY·CO·CY·CX. According to the author's views, the system C:C·CO·C:C has a greater additive power than C:C·CO·C, and the final product will be CX·CY·CO·C:C. Now Knoevenagel and Speyer (Abstr., 1902, i, 226) have shown that equal molecular quantities of distyryl ketone and ethyl acetoacetate yield a substance, $C_{23}H_{24}O_4$, which they formulate as CHPh:CH·CO·CH_2·CHPh·CH(CO_2Et)·COMe. Rabe and Elze (Abstr., 1902, i, 709) have shown that the substance has the constitution $CHPh{:}CH\cdot C(OH)\begin{<}\begin{matrix}CH_2\cdot CHPh\\ CH_2\text{---}CO\end{matrix}\end{>}CH\cdot CO_2Et$.

This constitution, which is confirmed by the author, is not a proof of the author's views, because even by the older theory the substance should be incapable of adding on a second molecule of ethyl acetoacetate, since it does not contain a carbonyl group in the immediate neighbourhood of the ethylenic linking. Similar cyclic β-ketone alcohols have been obtained from distyryl ketone and acetylacetone or benzoylacetone (the three β-ketone alcohols very easily lose a molecule of water, probably because the residual affinity of the nearer carbon atom in the ethylenic group renders the hydroxyl group more mobile by neutralising some of the affinity of the carbon atom to which it is attached). The author's view, however, is fully supported by the behaviour of ethyl benzoylacetate or ethyl malonate, which, even in excess, reacts with distyryl ketone to form the compounds

CHPh:CH·CO·CH_2·CHPh·CH(CO_2Et)·COPh

and CHPh:CH·CO·CH_2·CHPh·CH(CO_2Et)$_2$. Dianisylideneacetone, totramethyl-*pp'*-diaminodibenzylideneacetone, and dicinnamylideneacetone do not react with ethyl acetoacetate under the conditions in which distyryl ketone reacts so easily; benzylideneanisylideneacetone-*p*-dimethylaminodistyryl ketone, and benzylidenecinnamylideneacetone do combine with 1 mol. of ethyl acetoacetate, but less readily than distyryl ketone. It follows from these six examples that the groups OMe·C_6H_4·, NMe_2·C_6H_4·, and CHPh:CH· must in some way diminish the residual affinity, not only of the two external unsaturated carbon atoms, $\overset{\cdot\cdot}{\underset{\text{---O---}}{C:C\cdot\widehat{C\cdot C}:C}}$, but also of the carbonyl oxygen atom, the residual affinity of which influences the additive power of the two ethylenic linkings. The explanation in the case of dicinnamylideneacetone has been given above; in the cases of benzylideneanisylidene-

acetone and *p*-dimethylaminodistyryl ketone, the author suggests a distribution of the affinity represented in the annexed formula. The following compounds are described: Ethyl 3-phenyl-5-styryl-*cyclo*hexan-5-ol-1-one-2-carboxylate, prepared by Knoevenagel and Speyer (*loc. cit.*), is also obtained quantitatively when a mixture of distyryl ketone, ethyl acetoacetate, and a little piperidine is heated on the water-bath for a few hours and is then kept at the ordinary temperature. It is best converted into ethyl 3-phenyl-5-styryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate by heating its alcoholic solution with sodium ethoxide or piperidine. The *cyclo*hexene derivative yields a *benzyl* derivative, m. p. 128—129°, is converted by boiling glacial acetic and 20% sulphuric acids into 3-*phenyl*-5-*styryl*-Δ^5-cyclo*hexenone*, m. p. 110—111°, and by prolonged treatment with alcoholic sodium ethoxide is changed into an *isomeride*, m. p. 159°, of unknown constitution. *Ethyl α-benzoyl-γ-cinnamoyl-β-phenylbutyrate*, $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CHBz{\cdot}CO_2Et$, m. p. 134°, obtained quantitatively by keeping a mixture of distyryl ketone, ethyl benzoylacetate, and a little piperidine in ether for many days, forms a *dibromide*, m. p. 180°, and is decomposed into its generators by heating with 10% sodium hydroxide. Distyryl ketone, acetylacetone, and a little piperidine yield 2-*acetyl*-3-*phenyl*-5-*styryl*cyclo*hexan*-5-*ol*-1-*one*, $CHPh{:}CH{\cdot}C(OH)<^{CH_2\cdot CHPh}_{CH_2\text{---}CO}>CHAc$, m. p. 134—135°; a by-product of the reaction is 2-*acetyl*-3-*phenyl*-5-*styryl*-Δ^5-cyclo*hexenone*, m. p. 157—158°, which becomes the main product when the mixture is heated with alcohol for two to three days. 2-*Benzoyl*-3-*phenyl*-5-*styryl*-cyclo*hexan*-5-*ol*-1-*one*, m. p. 130°, and 2-*benzoyl*-3-*phenyl*-5-*styryl*-Δ^5-cyclo*hexenone*, m. p. 171°, are obtained when a mixture of distyryl ketone, benzoylacetone, and a little piperidine in alcohol is heated for two hours and for one day respectively. *Ethyl γ-cinnamoyl-β-phenylpropane-αα-dicarboxylate*, $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Et)_2$, m. p. 79°, obtained by heating a mixture of distyryl ketone, ethyl malonate, alcohol, and a little piperidine for two days on the water-bath, forms a *phenylcarbamic acid hydrazone*, m. p. 171°, and in alcoholic solution is hydrolysed by 25% sodium hydroxide at the ordinary temperature, yielding ultimately the free *acid*, m. p. 147—148° (decomp.), which is converted by heating into *γ cinnamoyl-β-phenylpropionic acid*, $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, m. p. 158—159°.

Benzylideneanisylideneacetone, ethyl acetoacetate, and a little piperidine yield *ethyl* 3-*phenyl*-5-p-*methoxystyryl*cyclo*hexan*-5-*ol*-1-*one*-2-*carboxylate*, m. p. 142°, which loses H_2O when heated with 10% sodium hydroxide, *ethyl* 3-*phenyl*-5-p-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 135°, being formed. p-*Dimethylaminodistyryl ketone*, m. p. 158°, which is best prepared by keeping a mixture of styryl methyl ketone, *p*-dimethylaminobenzaldehyde, and 10% sodium hydr-

oxide in 50% alcohol for a few weeks, reacts extremely slowly with ethyl acetoacetate in the presence of a little piperidine, yielding after seven days' heating a small quantity of a yellow, crystalline *substance*, m. p. 148°, which is presumably ethyl 3-phenyl-5-*p*-dimethylaminostyryl*cyclo*hexan-1-one-2-carboxylate; when heated for two hours with alcoholic sodium ethoxide, however, the two substances react to form ethyl 3-phenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate, which can only be isolated as the *benzoyl* derivative, m. p. 170—171°. A mixture of benzylidenecinnamylideneacetone, ethyl acetoacetate, and a little piperidine yields *ethyl* 3-*phenyl*-5-*β*-*styryl*-*vinyl*cyclo*hexan*-5-*ol*-1-*one*-2-*carboxylate*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}C(OH)\!<\!\begin{matrix}CH_2{\cdot}CHPh\\ CH_2\text{---}CO\end{matrix}\!>\!CH{\cdot}CO_2Et,$$

m. p. 144—145°, or *ethyl* 3-*phenyl*-5-*β*-*styrylvinyl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 145°, accordingly as it is heated on the water-bath for a day and kept for several days or is heated with alcohol for the same time. C. S.

Action of Hydroxylamine on Ketones of the Type CHR:CH·CH:CH·CO. Roberto Ciusa and A. Bernardi (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 58—62. Compare Abstr., 1907, i, 62).—Styryl methyl ketone yields the oxime of m. p. 117° already known; phenyl styryl ketone, two isomeric hydroxylamineoximes, which are also known. Benzylidenecinnamylideneacetone gives a *hydroxylamineoxime*, m. p. 165°. Benzylidenepyruvic acid yields an *oxime*, m. p. 168°. When the sodium salt of cinnamylidenepyruvic acid is acted on by hydroxylamine in the absence of sodium acetate, it yields the *sodium* salt of an *oxime*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}C(:NOH){\cdot}CO_2Na$, from which, by loss of carbon dioxide, cinnamylideneacetonitrile is formed. In the presence of sodium acetate, however, an *oxime*, $C_{28}H_{26}O_9N_2$, m. p. 216—218°, is produced, probably by the union of two molecules of the esterified acid with two molecules of hydroxylamine. Ethyl cinnamylidenepyruvate gives an *hydroxylamineoxime*, $C_{26}H_{34}O_9N_4$, m. p. 213°, formed from 2 mols. of ester and 4 mols. of hydroxylamine.

The formation of oximes in some cases, and of hydroxylamineoximes in others is due to the different velocities with which the addition of hydroxylamine proceeds at the carbonyl group and at the system of double linkings. If the former is the greater, an oxime is formed, which although unsaturated does not react with hydroxylamine. The velocity of oxime formation is diminished when a methyl group of the ketone is replaced by a phenyl group (Petrenko-Kritschenko, Abstr., 1906, ii, 341), and this explains the formation of oximes from styryl methyl ketone and cinnamylideneacetone (Abstr., 1907, i, 62), whilst phenyl styryl ketone and cinnamylideneacetophenone yield hydroxylamineoximes. R. V. S.

Displacement of Alkyl Groups under the Influence of Aluminium Chloride. Acetyldiphenylmethanes and their Derivatives. Constitution of Some Derivatives of Diphenylmethane. Henri Duval (*Bull. Soc. chim.*, 1910, [iv], **7**, 789—796, 796—800).—Most of the data published in these two papers have been

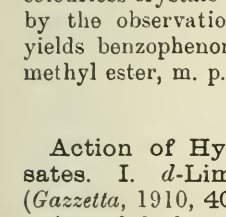
given already (Abstr., 1908, i, 277, 657). By the action of acetyl chloride on diphenylmethane in presence of aluminium chloride there is formed, in addition to 4-acetyl and 4 : 4′-diacetyl derivatives of the hydrocarbon, some acetophenone and a substance, m. p. 125°, which forms colourless crystals and appears to be a 4 : 4′-*diacetylbenzyldiphenylmethane*, $CH_2Ph\cdot C_6H_3Ac\cdot CH_2\cdot C_6H_4Ac$. Details of the method of carrying out the operation and of separating and purifying the products are given.

4-Acetyldiphenylmethane, b. p. 209—210°/15 mm., forms colourless crystals from alcohol.

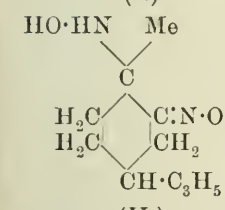
4 : 4′-Diacetyldiphenylmethane, b. p. 270—271°/15 mm., forms colourless crystals from warm alcohol. Its constitution is established by the observation that on oxidation with sodium hypobromite it yields benzophenone-4 : 4′-dicarboxylic acid, identified by means of its methyl ester, m. p. 231° (compare Limpricht, Abstr., 1900, i, 598).

T. A. H.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. I. *d*-Limonene-*o*-hydroxylamineoxime. Guido Cusmano (*Gazzetta*, 1910, 40, i, 602—613. Compare this vol., i, 182).—By the action of hydroxylamine on both *α*- and *β*-*d*-limonene bisnitrosochlorides, the same two *cis-trans*-isomeric hydroxylamineoximes (I. and II.) are obtained, and in addition a monoacidic base, $C_{10}H_{21}O_3N_3$. Whichever nitrosochloride is employed, one of the isomerides appears in excess of the other; it has a positive optical rotation, and is therefore called the *α*-form. Like the isomeride hydroxylaminocarvoxime (compare Harries and Mayrhofer, Abstr., 1899, i, 624), the two substances are soluble in acids and in alkalis, and reduce Fehling's solution in the cold, but they are stable towards nitrous acid, do not give oxidation products, and do not condense with aldehydes. In alkaline solution they are converted rapidly into a salt (decomposed by carbon dioxide) of an isomeric yellow compound, which is soluble in acids, but does not reduce Fehling's solution, and, moreover, gives a blue coloration with diphenylamine and a violet coloration with phenol. By the action of acids the compound is converted into the original hydroxylamineoxime.



(I.)



(II.)

α-Limonenehydroxylamineoxime hydrochloride, $C_{10}H_{16}O_2N_2,HCl,H_2O$, forms large, prismatic crystals, m. p. 142°, $[\alpha]_D^{27}$ −35·30°. When kept in a vacuum desiccator it loses a molecule of water, and then has m. p. 153° (decomp.). The free *α-hydroxylamineoxime*, $C_{10}H_{18}O_2N_2$, forms large, colourless, prismatic crystals, which soften towards 145° and decompose at 150°; it has $[\alpha]_D^{27}$ +17·73°. The *β-hydroxylamineoxime* is obtained in very small quantity along with the *α*-form. It has m. p. 173° (decomp.), and gives a *hydrochloride*, m. p. 152°. In the above preparation the *hydrochloride* of a base, $C_{10}H_{21}O_3N_3,HCl$, is also formed in small quantity. It crystallises in needles or flat prisms,

m. p. about 212° (decomp.); $[\alpha]_D^{27}$ −57·88°. The *base*, $C_{10}H_{21}O_3N_3$, has m. p. towards 210° (decomp.), and scarcely reduces Fehling's solution in the warm. All the above compounds are similarly obtained from *β-d*-limonene bisnitrosochloride. The yellow *isomeride* of the *α*-hydroxylamineoxime is readily formed from the latter substance, especially if impure or in solution. It is prepared by precipitating alkaline solutions of the substance with carbon dioxide. It has m. p. 167·5° (decomp.), and the molecular weight required by the formula $C_{10}H_{18}O_2N_3$. Treatment with acids converts it into the *α*-hydroxylamineoxime. When this change is effected with ethereal hydrogen chloride, a *substance*, $C_{10}H_{20}O_2N_2Cl_2$, is also obtained in yellow prisms, m. p. 130° (decomp. explosively). It is unstable, gives an intense blue diphenylamine reaction, does not dissolve in cold alkalis, and does not yield the hydroxylamineoxime when treated with hydrogen chloride in ether. R. V. S.

Mechanism of the Opening of the *cyclo*Butane Ring in Derivatives of Pinene. Guido Cusmano (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 63—68. Compare this vol., i, 574, and preceding abstract).—*α*-Pinenehydroxylamineoxime yields, with alkalis, nitrosopinene, with acids, hydroxydihydrocarvoxime. According to Wallach's theory of the mechanism of the opening of the *cyclo*butane ring in pinene and in sabinene derivatives (Abstr., 1908, i, 429), the formation of nitrosopinene as an intermediate product would be expected in the latter case, but the author shows that nitrosopinene does not yield hydroxydihydrocarvoxime when acted on by acids. Similarly, the salts of pinene*iso*nitroamineoxime yield, when treated with alkalis, both nitrosopinene and hydroxypinocamphoneoxime. Neither of these compounds can be converted into the other under the conditions of the experiment, but dilute acids transform hydroxypinocamphoneoxime into the isomeric hydroxydihydrocarvoxime. It appears, therefore, that Wallach's theory is untenable in this case, for which the author provides the explanation that the loss of the elements of water so disturbs the molecule as to cause rupture of the bridge at the same time, whilst the displacement of hyponitrous acid does not.

R. V. S.

Constitution of Fenchone. IV. Louis Bouveault and F. Levallois (*Bull. Soc. chim.*, 1910, [iv], 7, 807—810).—In previous papers (this vol., i, 572, 573, 627) the steps in the gradual degradation of fenchone to *apo*fenchene have been detailed, and in this communication an account is given of the oxidation of this hydrocarbon, on which a preliminary paper has been already published (Abstr., 1908, i, 193).

The products of the oxidation of *apo*fenchene by alkaline permanganate are (1) a neutral substance, probably a glycol; (2) a small quantity of a mixture of fatty acids, and acids possessing a pyruvic odour; (3) a mixture of acids (b. p. 70—160°/10 mm.) containing 90% of *iso*propylsuccinic acid, and (4) a mixture of acids (b. p. 160—165°/10 mm.). The fourth fraction contains three acids: (1) a hydroxy-acid, yielding on oxidation by lead peroxide and sulphuric acid a ketonic substance of the type R·COMe; (2) a ketonic acid, furnishing a *semi-*

carbazone, m. p. 140°, and (3) a ketonic acid, yielding a *semicarbazone*, $C_{10}H_{19}O_3N_3$, and which on oxidation with sodium hypobromite gives *β-iso*propylglutaric acid. As already indicated (*loc. cit.*), these results support Semmler's formula for fenchone. T. A. H.

Causes of Geranic Odours. Géza Austerweil and G. Cochin (*Compt. rend.*, 1910, **151**, 440—441. Compare this vol., i, 572).—The group :CH·CRR'·OH appears to be necessary for the presence of a geraniol odour. 1-*Methylgeraniol*, b. p. 105—106°/18 mm., prepared by the application of Grignard's reaction to citral, has a pronounced odour of pelargonium leaves; this is scarcely modified by the introduction of a second methyl group. 1 : 1-*Dimethylgeraniol*, b. p. 104°/16 mm., was obtained by oxidising the foregoing compound and submitting the ketone to Grignard's reaction. The odour of 1-ethylgeraniol and 1 : 1-*diethylgeraniol*, b. p. 123—125°/20 mm., resembles that of the primary alcohol. 1-iso*Butylgeraniol*, b. p. 115°/26 mm., and 1-*phenylgeraniol*, b. p. 135—138°/22 mm., have a less intense odour, that of the latter being somewhat rose-like. *Methyl*cyclo*geraniol*, b. p. 98°/20 mm., has scarcely any geraniol odour. W. O. W.

Oil of Copaiba. Ernst Deussen and Alfred Hahn (*Chem. Zeit.*, 1910, **34**, 873).—The caryophyllene from oil of copaiba is not a definite product, but yields on distillation several fractions with an increasing rotatory power, thus distinguishing it from the caryophyllene obtained from oil of cloves, the higher fractions of which show a decreasing rotatory power. No permanent blue coloration is obtained by acting on the caryophyllene from copaiba with nitrosyl chloride, whereas that from cloves yields a blue nitrosite.

Both oils, however, contain sesquiterpenes of a preponderating bicylic nature. L. de K.

Gurjun Oil (So-called East Indian Copaiba Oil). Ernst Deussen and Hans Phillipp (*Chem. Zeit.*, 1910, **34**, 921—923).—An investigation as to the nature of gurjun oil, which seems to belong to the series of sesquiterpenes.

Utz's statement that gurjun oil has a much higher boiling point than oil of copaiba is not quite correct, and this fact should be taken into consideration when testing copaiba balsam for gurjun balsam and operating, according to Utz, on the distillate. The colour reaction (whether working on the balsam itself or on the volatile oil therefrom) due to Turner and approved of by Utz, and again strongly recommended by the authors, is as follows: 3 to 4 drops of the sample of copaiba balsam are dissolved in 3 c.c. of glacial acetic acid, 1 drop of a 10% solution of sodium nitrite is added, and the mixture is carefully poured on to 2 c.c. of sulphuric acid. In presence of gurjun balsam a dark violet colour will be noticed in the acetic acid layer.

L. de K.

New Components of Oil of Jasmine Flower. F. Elze (*Chem. Zeit.*, 1910, **34**, 912).—In addition to the substances found in oil of jasmine flower by Hesse (Abstr., 1899, i, 377, 441; 1900, i, 48, 454;

1901, i, 220, 732), the author finds that it contains *p*-cresol and geraniol. L. DE K.

[Essential] Oil of Robinia Pseudocacia. F. ELZE (*Chem. Zeit.*, 1910, **34**, 814).—The author prepared a specimen of the oil by extracting the blossoms of the plant with very volatile solvents; the crude oil was then purified by treatment with alcohol. The oil had D^{15} 1·05, and the ester content calculated as methyl anthranilate amounted to 9%. The alcoholic solution had a distinct bluish fluorescence, and contained much indole. Under 5 mm. pressure, the oil passed over between 60° and 150°.

When submitted to the usual tests for essential oils, it was found to contain benzyl alcohol, α-terpineol, heliotropine, methyl anthranilate, linalool, indole, and ketone or aldehyde substances having the odour of peaches. The presence of nerol is also probable, and pyridine bases could be isolated. L. DE K.

Nerol and Farnesol in Java Canang Oil. F. ELZE (*Chem. Zeit.*, 1910, **34**, 851).—The oil contains about 0·2% of nerol and about 0·3% of farnesol. L. DE K.

Honduras Balsam. ALEXANDER TSCHIRCH and J. O. WERDMÜLLER (*Arch. Pharm.*, 1910, **248**, 420—430).—A pale Honduras balsam, represented by three samples having D 1·0886, 1·0905, and 1·0884 respectively, and a pronounced odour of storax, has mean acid number 32·67 and saponification number 173·2. The balsam is dissolved in ether and shaken with 1% sodium carbonate, whereby cinnamic acid is extracted together with an ester which yields cinnamic acid and honduroresinol by hydrolysis. The ethereal solution is next treated with 1% potassium hydroxide, whereby a further quantity of honduroresinyl cinnamate is obtained, and also a *substance*, $(C_{38}H_{38}O_4)_x$, which melts above 300°, does not respond to the phytosterol reactions, and shows the properties of a resin; it is called *β*-honduroresin. The ethereal solution is finally evaporated, leaving a yellow oil (so-called "cinnamëin") representing more than half the weight of the balsam. A portion of the oil yields by distillation cinnamic acid and an oil from which a small quantity of a hydrocarbon, *honduran*, C_8H_{10}, b. p. 154—155°, can be isolated. Another portion of the "cinnamëin" is hydrolysed by 1% potassium hydroxide, whereby cinnamyl alcohol, cinnamic acid, honduran, a *hydrocarbon*, $(C_3H_4)_x$, b. p. 140—155°, and distyrene are produced.

A dark Honduras balsam, represented by two samples, D 1·0897 and 1·0915, has acid number 29·9 and saponification number 153·9. It has been examined in the preceding way. The sodium carbonate extract contains cinnamic acid and the cinnamate of a *honduroresinol*, $(C_{16}H_{26}O_2)_x$, m. p. 141°. The potassium hydroxide extract contains cinnamic acid, honduroresinyl cinnamate, and a *resin*, m. p. 169—172°, which is not identical with *β*-honduroresin. The "cinnamëin" is hydrolysed by aqueous potassium hydroxide, and then distilled with steam. The non-volatile oil is dissolved in alcohol and cooled by solid carbon dioxide, whereby crystals are obtained, which are collected,

washed with alcohol, and treated with warm petroleum. The portion insoluble in the petroleum is a *resin*, m. p. 163°. When cooled in carbon dioxide, the petroleum solution deposits crystals of an unsaturated dihydric alcohol, *hondurol*, $C_{17}H_{16}O_2$, m. p. 42·5°, which forms a *dibenzoate*, m. p. 38°. The alcoholic mother liquor contains phenylpropyl alcohol and distyrene. C. S.

Cabureiba Balsam. Alexander Tschirch and J. O. Werdmüller (*Arch. Pharm.*, 1910, **248**, 431—432).—Schaer has recently described a rare balsam obtained from Brazil, and probably identical with Piso's cabureiba balsam (Guibourt's baume de Pérou brun or rouge en coques). Its ethereal solution yields to 1% sodium carbonate, benzoic (but not cinnamic) acid and a resinous substance, from which, after hydrolysis by 1% potassium hydroxide, benzoic acid, vanillin, and a *cabureibaresinotannol*, $C_{14}H_{18}O_4$, have been isolated. The balsam does not contain a "cinnamëin." C. S.

Benin Copal. M. Kahan (*Arch. Pharm.*, 1910, **248**, 433—442).—Benin copal is completely soluble in a mixture of ether and alcohol; alcohol alone dissolves about 60%, and ether 45·5%. The dried substance sinters at 120°, and forms a clear, transparent mass at 166°. It has acid number 101·15 (direct) and 118·75 (indirect), saponification number 134·4 (cold, after twenty-four hours), 143·5 (cold, after forty-eight hours), 149·8 (hot, after one hour), 146·3 (hot, after two hours), and iodine number 61·02. It does not yield succinic acid by dry distillation. An ethereal extract of Benin copal is shaken successively with 1, 2, and 5% ammonium carbonate, sodium carbonate, and potassium hydroxide; the residual solution, after removal of the ether, is distilled with steam, whereby an ethereal oil, b. p. 180—256°, and a yellow resin, *α-benincopaloresin*, m. p. 164—166°, are obtained. The ammonium carbonate extract contains *benincopalic acid*, $C_{17}H_{32}O_4$, m. p. 137°, acid number 183·4 (direct) and 180·6 (indirect), saponification number 194·6 (cold, after twenty-four hours), 196·0 (cold, after forty-eight hours), 196·7 (hot, after one hour), 200·2 (hot, after two hours), iodine number 83·43, which forms a lead salt insoluble in alcohol. The sodium carbonate extract contains *α-benincopalolic acid*, $C_{13}H_{32}O_6$, m. p. 81°, acid number 191·8 (direct) and 188·9 (indirect), saponification number 198·3 (cold) and 197·4 (hot), iodine number 87·24, and *β-benincopalolic acid*, $C_{20}H_{30}O_2$, m. p. 119°, acid number 185·2 (direct) and 184·1 (indirect), saponification number 193·3 (cold) and 194·6 (hot), iodine number 84·84; the lead salts of the two acids are insoluble in alcohol, but the former acid dissolves in glacial acetic acid. The potassium hydroxide extract contains *benincopalenic acid*, $C_{27}H_{48}O_2$, m. p. 101°, acid number 147·0 (direct) and 145·6 (indirect), iodine number 63·88.

The residue of Benin copal insoluble in ether is dissolved almost completely by a mixture of ether and alcohol. The solution, after being shaken with 1% potassium hydroxide, contains *β-benincopaloresin*, $C_{12}H_{30}O_{10}$, a white, amorphous substance. The potassium hydroxide extract contains *α-benincopalinic acid*, $C_{21}H_{30}O_3$, m. p. 187°, acid number 172·2 (direct) and 170·8 (indirect), saponification number 180·6 (cold) and 177·8 (hot), iodine number 76·51; *β-benincopalinic*

acid, $C_{15}H_{28}O_3$, m. p. 193—197°, acid number 216·3 (direct) and 216·3 (indirect), iodine number 97·79, and *γ-benincopaloresin*, $C_{13}H_{26}O_4$, m. p. 192—195°; the last is insoluble in alcohol, whilst of the two acids the former yields a lead salt which is insoluble in alcohol. C. S.

Accra Copal. M. Kahan (*Arch. Pharm.*, 1910, **248**, 443—450).—Accra copal is completely soluble in a mixture of ether and alcohol; alcohol alone dissolves about 54% and ether 50%. The substance has m. p. 106—156°, acid number 121·8 (direct) and 126·4 (indirect), saponification number 133·4 (cold) and 140·0 (hot), and iodine number 58·54.

An ethereal extract of Accra copal is shaken successively with ammonium carbonate, sodium carbonate, and potassium hydroxide; the residual solution contains *α-accracopaloresin*, $C_{15}H_{36}O_6$, m. p. 178—180°, and an ethereal oil, b. p. 164—266°. The ammonium carbonate extract contains *accracopalic acid*, $C_{21}H_{34}O_3$, m. p. 104—106°, acid number 177·5 (direct) and 175·0 (indirect), saponification number 180·7 (cold) and 180·6 (hot), iodine number 75·31. The sodium carbonate extract contains *α-accracopalolic acid*, $C_{18}H_{30}O_2$, m. p. 152—155°, acid number 194·6 (direct) and 192·5 (indirect), saponification number 195·3 (cold) and 196·4 (hot), iodine number 85·49, and *β-accracopalolic acid*, $C_{19}H_{32}O_2$, m. p. 144—148°, acid number 189·0 (direct) and 186·9 (indirect), saponification number 194·6 (cold) and 195·3 (hot), iodine number 86·86. The potassium hydroxide extract contains *α-accracopalenic acid*, $C_{10}H_{20}O_2$, m. p. 142—146°, and *β-accracopalenic acid*, $C_{12}H_{20}O_3$, m. p. 150—152°, acid number 246·4, which are separated by lead acetate.

The residue of the Accra copal insoluble in ether is dissolved in a mixture of ether and alcohol, and the solution is shaken with 1% potassium hydroxide; the ethereal alcoholic solution retains *β-accracopaloresin*, $C_{13}H_{26}O_3$, m. p. 197—199°, whilst the alkaline extract contains *accracopalinic acid*, $C_{14}H_{26}O_3$, m. p. 122—124°, acid number 214·9 (direct) and 214·2 (indirect), saponification number 226·8 (cold) and 228·2 (hot), iodine number 98·29, and *γ-accracopaloresin*, $C_{10}H_{20}O_3$, m. p. 184—186°, which is insoluble in alcohol. C. S.

Manila Copal. George F. Richmond (*Philippine J. Sci.*, 1910, [*A*], **5**, 177—201).—It is shown that the Manila copal produced in the Philippines is of two kinds, "recent" and semifossil," and is derived from a single species, *Agathis alba* (*Dammara orientalis*). The constants of the two kinds of resin are quite similar, and they both consist of a mixture of resin acids with a lactone (?), neutral unsaponifiable resin, and more or less volatile oil. The only well-defined solid product obtained from the resin is a crystalline acid of the formula $C_{10}H_{15}O_2$. On distillation in steam the resin yields volatile oil in quantity, which depends partly on the age of the resin and partly on its physical condition. The volatile oil, D_4^{15} 0·865, n_D^{30} 1·4648, $[\alpha]_D^{30}$ −26·55°, contains pinene. The resin dissolves completely in alcohol, and addition of potassium hydroxide to such a preparation yields (*A*) a solution containing volatile oil and soluble

potassium resinates, and (*B*) a precipitate containing insoluble potassium resinates and some neutral resin.

From *A* the following substances were obtained: (1) a lemon-yellow, volatile oil possessing a terpene-like odour; (2) an *acid*, $C_{10}H_{15}O_2$, m. p. 185—187°, which is dextrorotatory and crystallises from dilute alcohol in colourless needles, and (3) an amorphous *acid*, $C_{22}H_{34}O_4$, which can be distilled almost unchanged at a pressure of 3—5 mm., yielding a clear, amber-coloured product.

From *B* there were isolated (1) an amorphous *acid*, $C_{32}H_{50}O_4$, m. p. above 220°; (2) a *lactonic* substance, which on digestion with hot aqueous solutions of potassium hydroxide furnishes the potassium salt of a resin acid similar to that yielding the insoluble resinate referred to above, and (3) neutral unsaponifiable resin. These results, especially as regards the properties of the acids, are not in accordance with those recorded by Tschirch and Koch for Manila copal derived from *Dammara orientalis* (Abstr., 1902, i, 478).

On dry distillation the copal yielded about 70% of greenish-yellow oil, b. p. 140—350°, and left a pitch-like residue (compare succeeding abstract). On "melting" various samples of the resin at temperatures ranging from 250—325°, the loss varied from 13·3 to 17·4%. The "melted" resin was similar in composition to the raw material, but contained less neutral resin, so that the latter only appears to undergo change in the ordinary process of making copal varnish. The remainder of the paper deals with copal varnish manufacture.

T. A. H.

Destructive Distillation of Manila Copal. Benjamin T. Brooks (*Philippine J. Sci.*, 1910, [*A*], 5, 203—217. Compare preceding and succeeding abstracts).—On heating, Manila copal froths until the temperature reaches 330°, when the resin melts and quiet ebullition sets in. Up to 330° the products evolved include resin oil, pinene, *β* pinene, limonene, dipentene, camphene, water, formic and acetic acids, methyl alcohol, acetone, formaldehyde, pyruvaldehyde, furfuraldehyde, carbon dioxide, acraldehyde (?), and saturated and unsaturated hydrocarbons. Above 330°, considerable quantities of carbon monoxide and some ethylene and propylene are formed, but the other products of this further stage in destructive distillation were not studied. The remainder of the paper deals with (1) the effect of heat in rendering Manila copal soluble and suitable for varnish manufacture, and (2) its behaviour with various solvents.

T. A. H.

Oxidation of Manila Copal by the Air. Benjamin T. Brooks (*Philippine J. Sci.*, 1910, [*A*], 5, 219—227. Compare two preceding abstracts).—The well-known fact that the older copal resins ("fossil" copals) are better suited for varnish manufacture than the "recent" kinds has led the author to investigate the changes which take place when Manila copal is exposed to air and light. The results show that the resin absorbs oxygen somewhat rapidly, forming organic peroxides (compare Fahrion, Abstr., 1902, i, 165; 1904, i, 332; 1907, i, 329), and evolves carbon dioxide, formaldehyde, formic acid, and hydrogen

peroxide. The evolution of carbon dioxide is probably due to the formation and subsequent decomposition of peroxides, both in the cases of Manila copal and colophony. These changes are accompanied by an increase in the Koettstorfer number of the resin. The change in the Koettstorfer number, which accompanies prolonged maceration of many resins in potassium hydroxide in alcohol, is, however, not due to oxidation effects during the experiment, but probably to the gradual saponification of lactones and the breaking down of organic peroxides. The oxidation of Manila copal is accelerated by sunlight. Under certain conditions the resin gives off vapours which affect a photographic plate. The mixed resin acids of Manila copal show similar changes on exposure to air, but more slowly. T. A. H.

Oleo-Resin of Pinus insularis. Benjamin T. Brooks (*Philippine J. Sci.*, 1910, [*A*], 5, 229—231).—The turpentine oil distilled from this oleo-resin had D_{30}^{30} 0·8593, n_D^{30} 1·4656, $[\alpha]_D$ +26·5 at 30°, distilled to the extent of 96% between 154° and 165·5°, and consisted mainly of pinene.

The colophony left on distillation of the oleo-resin consisted almost entirely of abietic acid, m. p. 154—156°, had Koettstorfer number 170·2, and gave the Liebermann-Storch reaction. T. A. H.

Preparation of True Arbutin. Henri Hérissey (*Compt. rend.*, 1910, 151, 444—447; *J. Pharm. Chim.*, 1910, [vii], 2, 248—253).—Fifteen grams of commercial arbutin (containing methylarbutin) are dissolved in 95% alcohol (500 c.c.) and treated with 10 grams of potassium hydroxide in 125 c.c. of alcohol. When clear, the supernatant liquid is removed, and the crystalline precipitate washed with alcohol (20 c.c.), dissolved in 75 c.c. of boiling alcohol and acetic acid (7 c.c.), and treated with calcium carbonate (5 grams). After removing the alcohol, the residue is lixiviated with water (100, 50, and 50 c.c.). The filtrate is treated with calcium carbonate (2 grams), evaporated to dryness, and the product crystallised from ethyl acetate. Pure arbutin crystallises with $1H_2O$, and is identical with the glucoside obtained from the pear tree by Bourquelot (this vol., ii, 742). The anhydrous substance has $[\alpha]_D$ −63·45°. W. O. W.

A New Glucoside Hydrolysed by Emulsin in Menyanthes trifoliata. Marc Bridel (*J. Pharm. Chim.*, 1910, [vii], 2, 165—167).—The glucoside, which it is proposed to call *meliatin*, m. p. 222° (corr.), $[\alpha]_D$ −81·94° in alcohol, is crystalline. Its solutions are hydrolysed by emulsin, becoming bluish-green and dextrorotatory, and producing a reducing sugar. It is not identical with Kromayer's menyanthin (*Arch. Pharm.*, 1865, 174, 35, and Lendrich, Abstr., 1892, 1262). T. A. H.

The Chlorophyll Group. VII. Chlorophyllan, *allo*Chlorophyllan, and Chlorophyllpyrrole. Henryk Malarski and Leon Marchlewski (*Biochem. Zeitsch.*, 1910, 27, 246—260. Compare this vol., ii, 362).—It is claimed that the substances described under the name of chlorophyllan, phyllogen, and phæophytin are identical.

They were prepared by the methods described by Schunk and Marchlewski and Willstätter, and the various preparations yielded the same amount of phytol on hydrolysis, and yielded chlorophyllanic acids similar to the phytochlorins of Willstätter. A preparation was also obtained which did not agree in properties with Willstätter's phytochlorin *d*. Chlorophyllan also contains in small quantities (especially that derived from maple leaves) another product, *allo*-chlorophyllan, of which the authors give some spectrum absorption measurements. They have also succeeded in preparing from chlorophyllpyrrole, azo-colouring matters with benzenediazonium chloride identical with those obtained from hæmopyrrole. S. B. S.

Benzoyleuxanthone. Ernst Zerner (*Monatsh.*, 1910, 31 797—798).—Graebe and Ebrard (Abstr., 1882, 1301) describe dibenzoyleuxanthone as yellow or brown, m. p. 214°. On benzoylating euxanthone with benzoyl chloride and potassium hydroxide, the dibenzoyl derivative is obtained colourless, m. p. 221—222° (corr.), together with about 10% of yellow *monobenzoyleuxanthone*, m. p. 156—159° (corr.), in which the benzoyl group occupies position 7. On benzoylating in acid solution, only dibenzoyleuxanthone results. E. F. A.

[**Preparation of Halogen Derivatives of 6-Amino-3-keto-(1)-thionaphthen and Nitroisatins.**] Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 221529 and 221530).—When the products obtained by condensing 6-amino-3-keto-(1)-thionaphthen in acetic acid solution with nitroisatins or amino-oxindoles are treated with halogens either with or without previous reduction, brownish-yellow dyes are obtained.

6-Amino-3-keto-(1)-thionaphthen, m. p. 165°, is a brownish-grey powder, soluble in hot water.

The nitration of isatin with fuming nitric acid (D 1·5) yields a *nitroisatin*, which crystallises from acetic acid in yellow needles, m. p. 253—255°; potassium nitrate with concentrated sulphuric acid may also be employed, but under these conditions the product has m. p. 248—250°.

The second patent deals with the products obtained when the 6-amino-3-keto-(1)-thionaphthen in the foregoing condensation is replaced by *m*-acetylaminophenylthioglycol-*o*-carboxylic acid, the components being heated together during three hours in the presence of acetic anhydride; the *product* is a brown powder, which becomes yellow on treatment with sodium hyposulphite, and on halogenation yields vat dyes. The reduction of these compounds previous to halogenation is also described in the patents. F. M. G. M.

Ergoxanthein. William T. Wenzell (*Amer. J. Pharm.*, 1910, 82, 410—416).—The author does not consider that the preparation of the alkaloids of ergot in a purer form justifies the supersession of the names ecboline and ergotine originally applied by him to these alkaloids (*Amer. J. Pharm.*, 1864, 36, 193; compare Kobert, Abstr., 1885, 821; Barger, Trans., 1907, 91, 337, and Barger and Dale, Abstr., 1907, i, 79).

Ergoxanthein was prepared from Squibb's fluid extract of ergot by shaking this with ether after preliminary purification with alcohol and chloroform. It is an orange-yellow, amorphous substance, giving blood-red solutions with alkalis, developing a deep orange colour with nitric acid and a blood-red coloration with sulphuric acid. It gives an orange-yellow precipitate with lead acetate and a yellow precipitate with phosphotungstic acid. The absorption spectra of solutions of ergoxanthein are recorded which may be of value for the estimation and toxicological detection of ergot. The substance is physiologically active, and causes a rise in blood pressure. T. A. H.

Hydroxylupanine. A. Beckel (*Arch. Pharm.*, 1910, **248**, 451—457).—The properties and behaviour of natural hydroxylupanine, already recorded by Bergh (*Arch. Pharm.*, 1904, **242**, 416) are confirmed, and the formation of *d*-lupanine by reduction is proved conclusively by an examination of the aurichloride, platinichloride, and thiocyanate. C. S.

Compounds of α-Naphthylcarbamide with some Physiologically Important Substances. Carl Neuberg and Else Hirschberg (*Biochem. Zeitsch.*, 1910, **27**, 339—347).—This reagent gives sparingly soluble α-naphthylhydantoic acids with amino-acids, and α-naphthylurethanes with alcohols and phenols. The former can be prepared by shaking aqueous solutions of the reacting substance together in the presence of alkalis; the latter must be prepared in absence of water, and are obtained by heating the reacting substances together. The following substances were obtained: *glyceryl tri-α-naphthylcarbamate*,

$C_{10}H_7\cdot NH\cdot CO_2\cdot CH_2\cdot CH(CO_2\cdot NH\cdot C_{10}H_7)\cdot CH_2\cdot CO_2\cdot NH\cdot C_{10}H_7$,

m. p. 279—280°; the *di-α-naphthylurethane* of glyceric acid,

$C_{10}H_7\cdot NH\cdot CO_2\cdot CH_2\cdot CH(CO_2H)\cdot CO_2\cdot NH\cdot C_{10}H_7$,

m. p. 289—290°; *phenyl α-naphthylcarbamate*, m. p. 136—137°; *o-tolyl α-naphthylcarbamate*, m. p. 145°; *m-tolyl α-naphthylcarbamate*, m. p. 135—136°; *p-tolyl α-naphthylcarbamate*, m. p. 150—151°; *carvacryl α-naphthylcarbamate*, m. p. 287—288°; *saligenyl α-naphthylcarbamate*, m. p. 283°; *cinnamyl α-naphthylcarbamate*, m. p. 119—120°; *menthyl α-naphthylcarbamate*, m. p. 128°; *l-bornyl α-naphthylcarbamate*, m. p. 132°; *isobornyl α-naphthylcarbamate*, m. p. 129°; *α-terpinyl α naphthylcarbamate*, m. p. 151—152°; *cyclohexyl α-naphthylcarbamate*, m. p. 139—140°; *furfuryl α-naphthylcarbamate*, m. p. 133°; *cholesteryl α-naphthylcarbamate*, m. p. 175—176°; *α-naphthylcarbamo-d-glucosamine*, $OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot CH(CHO)\cdot NH\cdot CO\cdot NH\cdot C_{10}H_7$, m. p. 234—236°; *α-naphthylcarbamidoacetaldehyde*,

$C_{10}H_7\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CHO$,

amorphous. S. B. S.

Substituted Rodanic Acids and their Aldehyde Condensation Products. X. Rudolf Andreasch (*Monatsh.*, 1910, **31**, 785—795. Compare Abstr., 1908, i, 683).—*Ammonium dithiocarbaminoacetate*,

$NH_4\cdot S\cdot CS\cdot NH\cdot CH_2\cdot CO_2\cdot NH_4$,

prepared by the interaction of glycine, carbon disulphide, and alcoholic ammonia, forms colourless needles, m. p. 110° (decomp.).

Ammonium-α-dithiocarbaminopropionate, prepared in a similar manner from alanine, has m. p. 128—129° (decomp.). It reacts with ethyl chloroacetate, forming *α-rhodanine propionic acid,*

$$CO_2H\cdot CHMe\cdot N<\begin{matrix}CS\cdot S\\ |\\ CO\cdot CH_2\end{matrix}>,$$

separating in granular crystals, m. p. 147°. Condensation products with aldehydes are formed on heating the components in acetic acid.

β-Benzylidene-α-rhodanine propionic acid forms bright yellow granules or needles, m. p. 191°. *β-Dimethylaminobenzylidene-α-rhodanine propionic acid* forms a crust of dark reddish-brown crystals, m. p. 210—220°; it dyes the skin, wool, and silk orange-red, but the colour is not fast. *β-p-Hydroxybenzylidene-α-rhodanine propionic acid* forms a crust of light chrome-yellow needles, which sinter at 190°, m. p. 205—210°, forming a red sublimate.

β-Methylenedioxybenzylidene-α-rhodanine propionic acid, prepared by condensation with piperonal, forms orange-yellow granules or a yellow, crystalline powder, m. p. 197—199°.

Rhodanineglycylglycine, $CO_2H\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot N<\begin{matrix}CS\cdot S\\ |\\ CO\cdot CH_2\end{matrix}>$, is prepared by the interaction of glycylglycine, ammonia, and carbon disulphide, the corresponding *dithiocarbamate* being first formed and immediately condensing with ethyl chloroacetate. A honey-yellow syrup was obtained, which condensed with benzaldehyde to *benzylidene-rhodanineglycylglycine.* It crystallises in greenish-yellow plates or needles, m. p. 190° (sinters at 180°).

In the case of asparagine, aspartic and glutamic acids, and leucine, both the rhodanines and their aldehyde condensation products could only be obtained as syrups. E. F. A.

Formation of Imino-ethers by Direct Alkylation of Acid Amides with Methyl Sulphate. Motooki Matsui (*Mem. Coll. Sci. Eng. Kyoto,* 1909—1910, **2**, 37—45).—Imino-ethers may be obtained directly from the free acid amides by alkylation with methyl sulphate at temperatures below 100°, showing that the amide itself may react in the iminohydrin form, just as does its silver salt. Both aliphatic and aromatic acid amides, as well as the thio-acid amides, react in this way, giving rise to the methyl hydrogen sulphates of the imino-ethers. These compounds generally separate as an oil, which may afterwards crystallise, when the amide is heated in a reflux apparatus with methyl sulphate. In some cases the imino-ether was set free by treatment with sodium carbonate solution, extracted with ethyl ether, and the hydrochloride or other salts prepared.

Thiobenziminomethyl ether methyl hydrogen sulphate, C_8H_9NS,HSO_4Me, and *thio-p-toluiminomethyl ether methyl hydrogen sulphate,*

$$C_9H_{11}NS,HSO_4Me,$$

were prepared from thiobenzamide and thio-*p*-toluamide respectively; they form long, colourless prisms. The free ethers separated as an oil on the addition of sodium carbonate solution, but could not be isolated, as they decompose into methyl mercaptan and cyaphenine or cyatoline.

Benziminomethyl ether methyl hydrogen sulphate was obtained from

benzamide as a deliquescent substance; it could not be purified from the admixed benzamide. The hydrochloride (Abstr., 1895, i, 522) and also the *platinichloride*, $(C_8H_{10}ON)_2PtCl_6$, were prepared.

o-Nitrobenziminomethyl ether, $C_8H_9O_3N_2$, was obtained from *o*-nitrobenzamide in colourless crystals, m. p. 87°. The *hydrochloride* forms slender needles, m. p. 164—165°; the *platinichloride*,

$$(C_8H_9O_3N_2)_2PtCl_6,$$

m. p. 162°, was also prepared. The hydrochloride was transformed into *o-nitrobenzamidine*, which is a yellow liquid of alkaline reactions; its *platinichloride*, $(C_7H_8O_2N_3)_2PtCl_6$, was analysed.

Benzphenyliminomethyl ether, $C_9H_{12}ON$, was obtained from acetanilide as a colourless, viscid oil. The *hydrochloride* is decomposed by water; the *platinichloride*, $(C_9H_{12}ON)_2PtCl_6$, was analysed.

Formamide gave rise to hygroscopic, scaly crystals of *formiminomethyl ether methyl hydrogen sulphate*, from which formiminomethyl ether was liberated by alkali. *Acetiminomethyl ether* is an oil, b. p. 63—65°. Qualitative proof of the formation of *propioiminomethyl ether* from propionamide was obtained. T. S. P.

Methylpyridonium Picrate. G. Totani and Z. Hoshiai (*Zeitsch. physiol. Chem.*, 1910, 68, 85. Compare Abstr., 1909, ii, 327).—*Methylpyridonium picrate*, $C_5H_5NMe\cdot O\cdot C_6H_2(NO_2)_3$, crystallises from water in slender, yellow needles, m. p. 212°. Its solubility in 100 parts of solvent at the ordinary temperature is: water 1·092, alcohol 0·368, ether 0·017. J. J. S.

[Preparation of Dinitronaphthylpyridinium Derivatives.] Farbenfabriken vorm. Freidr. Bayer & Co. (D.R.-P. 222130. Compare Zincke, Abstr., 1904, i, 448).—The interaction of secondary dihydroindoles with cyanopyridinium or dinitrophenylpyridinium salts, whereby red to violet basic dyes are obtained, has previously been recorded. When the halogen-free *product*, red needles, m. p. 214°, prepared by the action of pyridine (2 mols.) on 1-chloro-2 : 4-dinitronaphthalene (1 mol.) in aqueous alcoholic solution, is treated with α-methyldihydroindole in glacial acetic acid, and hydrochloric acid dropped in, a mixture of 2 : 4-dinitro-α-naphthylamine and a dye is obtained; these are separated by extracting the latter with boiling water, and subsequently precipitating with salt; it forms a brownish-red powder. F. M. G. M.

Racemic Liquid Compounds. Albert Ladenburg (*Compt. rend.*, 1910, 151, 283—284).—Four crystallisations of the *d*-camphor sulphonate of *r*-pipecoline suffice to obtain the *l*-base in a state of purity. The author shows that the freezing-point curve for mixtures of *d*- and *l*-pipecoline agrees with the existence of a racemic liquid form of this substance. W. O. W.

[Preparation of Anthraquinoneacridones.] Fritz Ullmann (D.R.-P. 221853).—When the anilinoanthraquinonecarboxylic acids of general formula $CO_2H\cdot C_6H_4\cdot NHR$ (where R = anthraquinone or a substituted anthraquinone residue) are treated with reagents, such as

phosphorus pentachloride and aluminium trichloride, they are converted into anthraquinoneacridones.

Anthraquinoneacridone is prepared by treating α-anilinoanthraquinonecarboxylic acid (obtained from α-nitro- or α-chloro-anthraquinone and anthranilic acid) with phosphorus pentachloride in benzene solution, and heating the red *acid chloride* thus obtained with aluminium trichloride; it crystallises from aniline in violet-red, glistening needles with a metallic lustre; its solution in concentrated sulphuric acid is red.

The *methylanthraquinoneacridone* prepared from the condensation product of anthranilic acid with 1-chloro-4-methylanthraquinone has similar properties.

The *product* obtained by treating β-anilinoanthraquinonecarboxylic acid (prepared from β-aminoanthraquinone and *o*-chlorobenzoic acid) with concentrated sulphuric acid is a very sparingly soluble, yellow powder, which dissolves in concentrated sulphuric acid with a brownish-yellow colour. F. M. G. M.

New Group of Substituted Dioxindoles. Moritz Kohn (*Monatsh.*, 1910, 31, 747—751).—Isatin reacts with the Grignard reagent, only one of the carbonyl groups being affected, and on hydrolysis compounds of the type $C_6H_4<^{CR(OH)}_{NH---}>CO$ are obtained.

The *phenyl* derivative forms long, white, lustrous needles, m. p. 213°, to a yellowish-brown liquid.

The *benzyl* derivative crystallises in colourless needles, m. p. 171—173°.

The *α-naphthyl* derivative becomes coloured above 200°, m. p. 233°.

The p-*bromophenyl* derivative separates in wool-like needles, m. p. 193—195° (decomp.). All these substituted dioxindoles are stable in the atmosphere. E. F. A.

Conversion of Stachydrine into the Isomeric Methyl Hygrate. Georg Trier (*Zeitsch. physiol. Chem.*, 1910, 67, 324—331. Compare Willstätter, Abstr., 1902, i, 266; Willstätter and Kahn, *ibid.*, 1904, i, 235, 560).—When distilled under reduced pressure, stachydrine (this vol., ii, 743) gives a 66% yield of the isomeric methyl hygrate,

$$CH_2<^{CH_2\cdot CH---CO}_{CH_2\cdot NMe_2\cdot O} \rightarrow CH_2<^{CH_2\cdot CH\cdot CO_2Me}_{CH_2\cdot NMe}.$$

Other products are trimethylamine and a little hygric acid.

So far it has not been found possible to transform the methyl ester into stachydrine. The *aurichloride* of the methyl ester,

$$C_7H_{14}O_2NAuCl_4,$$

crystallises in rectangular plates, m. p. 84—86°, and when boiled with excess of hydrochloric acid yields hygric acid aurichloride.

When the hydrochloride of the ethyl ester of stachydrine (containing also stachydrine hydrochloride) is distilled, the products are hygric acid, its methyl and ethyl esters, and their decomposition products.

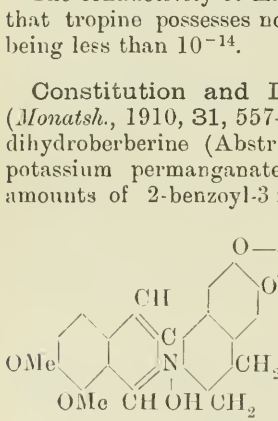
Hygric acid is non-poisonous, whereas its methyl ester is a strong poison. J. J. S.

Dissociation Constant of Tropine and its Variation with Temperature. HARALD LUNDÉN (*J. Chim. Phys.*, 1910, 8, 331—336).—The molecular conductivities of solutions of tropine hydrochloride at 10°, 25°, and 50° show that tropine is a fairly strong base, so that hydrolytic dissociation of the hydrochloride does not occur. The molecular conductivity of free tropine at infinite dilution is calculated to be 0·17 at 10°, 0·227 at 25°, 0·326 at 50°. The variation of conductivity of the hydrochloride with temperature is in agreement with Johnston's logarithmic theorem (Abstr., 1909, ii, 854).

The dissociation constant of tropine calculated from measurements on the free base is $1{\cdot}87 \times 10^{-4}$ at 10°, $2{\cdot}74 \times 10^{-4}$ at 25°, and $3{\cdot}89 \times 10^{-4}$ at 50°. These figures are of an entirely different order from that obtained by Veley by the colorimetric method, namely, $1{\cdot}10^{-9}$ at 17° (Trans., 1909, 95, 3). They are, however, of the same order as the dissociation of piperidine ($1{\cdot}6.10^{-3}$ at 25°) and coniine ($1{\cdot}3.10^{-3}$ at 25°), to which tropine is allied. The heat of dissociation of tropine calculated from the dissociation constant is negative, but appreciably greater than the negative heat of dissociation of piperidine.

The conductivity of mixtures of sodium hydroxide and tropine shows that tropine possesses no acidity, its constant of acidic dissociation being less than 10^{-14}. R. J. C.

Constitution and Derivatives of Berberine. FRANZ FALTIS (*Monatsh.*, 1910, 31, 557—581).—When Freund and Beck's α-phenyldihydroberberine (Abstr., 1905, i, 151) is repeatedly oxidised with potassium permanganate at the ordinary temperature, appreciable amounts of 2-benzoyl-3 : 4-dimethoxybenzoic acid are formed. This reaction supports the formula (annexed formula) suggested several years ago (Abstr., 1906, i, 979) and supported recently by Perkin (Trans., 1910, 97, 321). If berberine had the constitution originally suggested by Perkin, the product of oxidation would be 2-benzoyl-5 : 6-dimethoxybenzoic acid.



2-Benzoyl-3 : 4-dimethoxybenzoic acid, $C_6H_2Bz(OMe)_2{\cdot}CO_2H$, crystallises in colourless needles, m. p. 190—191°, and is not decomposed when heated with concentrated hydrochloric acid at 150°. Its constitution follows from the fact that, when fused for two minutes with potassium hydroxide, the products are benzoic and protocatechuic acids. Boiling hydriodic acid converts the benzoylated acid into a *compound*, $C_{27}H_{20}O_8$, m. p. 223—224°. This is probably an additive compound of the 3 : 4-dihydroxy-2-benzoylbenzoic acid with 2 : 3-dihydroxybenzophenone. An impure *4-hydroxy-2-benzoyl-3-methoxybenzoic acid*, $C_{15}H_{12}O_5$, is formed when hydrogen chloride is led through a suspension of the dimethoxy-acid in boiling hydrochloric acid for twenty-four hours.

Gadamer (Abstr., 1902, i, 555; 1905, i, 369) states that the reaction between berberine and potassium hydroxide solution is analogous to that between benzaldehyde and alkali, and that the products are

dihydroberberine and oxyberberine. The author claims that the reaction is similar to that between quinoline methiodide and alkali (Decker, Abstr., 1903, i, 516, 718), and that the products are oxyberberine and tetrahydroberberine. The reduction product differs from pure tetrahydroberberine (m. p. 167·5—168·5°) prepared from berberine by the action of zinc dust and glacial acetic acid; (*a*) its hydrochloride contains water of hydration, and (*b*) it is more readily transformed into berberine, for example, when its hydrochloride is heated at 100°.

The golden-yellow colour of Gadamer's oxyberberine is completely removed when the product is heated with zinc dust and glacial acetic acid. It is then obtained in glistening, colourless needles, m. p. 200—200·5°, with all its other properties intact. It would thus appear that only those berberine derivatives which contain a non-hydrogenated pyridine ring are coloured.

Oxyberberine hydrochloride and *hydrobromide* are readily obtained as lemon-yellow, amorphous precipitates when hydrogen chloride or bromide is passed into a chloroform solution of the base, but immediately yield colourless oxyberberine when treated with water. The hydrochloride, $C_{20}H_{17}O_5N,HCl$, softens at 200°, and melts at about 240°. The *stannichloride*, $C_{20}H_{17}O_5N,HCl,SnCl_4$, forms a stable, yellow, amorphous precipitate.

Methylnoroxyberberine, $C_{19}H_{15}O_5N$, obtained by passing hydrogen chloride into a boiling glacial acetic acid solution of oxyberberine or by heating oxyberberine hydrobromide in boiling xylene, crystallises in glistening, silky needles, m. p. 248°. It does not yield salts, and gives an intense violet-blue coloration with 50% sulphuric acid and a drop of nitric acid.

A black powder is formed when oxyberberine is boiled for a long time with hydriodic or hydrobromic acid. Methylnoroxyberberine contains a hydroxy-group, and yields an *acetyl* derivative, $C_{21}H_{17}O_6N$, m. p. 242—244°.

Bromomethylnoroxyberberine, $C_{19}H_{14}O_5NBr$, prepared by the action of bromine on a chloroform solution of methylnoroxyberberine, crystallises from hot xylene in slender needles, m. p. 239° (decomp.), and yields an *acetyl* derivative, $C_{21}H_{16}O_6NBr$, m. p. 225—227° (decomp.).

Bromine reacts with a chloroform solution of oxyberberine, yielding *bromo-oxyberberine tribromide*, $C_{18}H_{10}O_3NBr(OMe)_2,HBr,Br_2$, as golden-yellow needles, m. p. 210° (decomp.).

The tribromide when boiled with xylene yields bromomethylnoroxyberberine, and when treated with water yields *bromo oxyberberine*, $C_{20}H_{16}O_5NBr$, which crystallises from alcohol in large, colourless prisms, m. p. 184—185°. J. J. S.

Conversion of Hydrazidines into Hydrazines. Giacomo Ponzio (*Gazzetta*, 1910, **40**, i, 433—435).—The hydrazidines previously described (this vol., i, 443) when heated for some hours with dilute acids (10%) evolve ammonia, and are converted into the corresponding acylarylhydrazines; thus ω-aminobenzaldehyde-*o*-nitrophenylhydrazone (*loc. cit.*) yields benzoyl-*o*-nitrophenylhydrazine,

$$COPh\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2.$$

This reaction forms an argument for the formula $NH_2{\cdot}CR{:}N{\cdot}NH_2$ in preference to $NH{:}CR{\cdot}NH{\cdot}NH_2$ for the hydrazidines. R. V. S.

Benzylidenehydrazines. Hartwig Franzen and Th. Eichler (*J. pr. Chem.*, 1910, [ii], 82, 241—251).—At high temperatures or in boiling xylene, benzylidenehydrazines of the type $CHR{:}N{\cdot}NH_2$ react as such or decompose into aldazines and hydrazine, the latter of which then attacks one or more of the other substances present; for example, benzylidenehydrazine and phthalimide at 130—140° or in boiling xylene yield benzaldazine and phthalhydrazide; benzyldenehydrazine and carbon disulphide form benzaldazine and hydirazine dithiocarbazinate, the latter being obtained by the action of hydrazine and carbon disulphide; benzylidenehydrazine and ethyl benzoate at 160—170° yield benzaldazine, benzhydrazide, and benzylidenebenzhydrazide; benzylidenehydrazine, benzoyl chloride, and pyridine in dry ether at 0° yield benzaldazine, benzylidenebenzhydrazide, and dibenzhydrazide.

The following benzylidenehydrazines are prepared by Curtius and Franzen's method of treating aldazines with a boiling solution of hydrazine hydrate: m-*Hydroxybenzylidenehydrazine*,

$$OH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH_2,$$

m. p. 104·5° (*picrate*, m. p. 187°; *phenylthiosemicarbazide*, m. p. 194°), from m-*hydroxybenzaldazine*, m. p. 205°; p-*hydroxybenzylidenehydrazine*, m. p. 139° (*picrate*, m. p. 222°; *phenylthiosemicarbazide*, m. p. 225°), from p-*hydroxybenzaldazine*, m. p. 232°; o-*aminobenzylidenehydrazine*, m. p. 62° (*dipicrate*, m. p. 188°), from *o*-aminobenzaldazine; m-*methoxybenzylidenehydrazine*, b. p. 174—175°/21 mm. (*phenylthiosemicarbazide*, m. p. 153°), from *m*-methoxybenzaldazine; *p*-methoxy- and *p*-ethoxy-benzaldazines yield the corresponding benzylidenehydrazines, which, however, revert to the original benzaldazines during the process of isolation by ether. *Heptylidenehydrazine*,

$$CH_3{\cdot}[CH_2]_5{\cdot}CH{:}N{\cdot}NH_2,$$

b. p. 164—165°/12 mm., was prepared from heptaldehyde and aqueous hydrazine hydrate.

The water formed during the production of mixed aldazines by the condensation of benzylidenehydrazines and aldehydes complicates the reaction by attacking the benzylidenehydrazine, whereby a second aldazine is formed and hydrazine hydrate, which then reacts with the aldehyde to produce a third aldazine. The authors prevent the by-reactions by using, instead of the aldehyde, its condensation product with aniline; thus, benzylidenehydrazine and ethereal *m*-nitrobenzylideneaniline yield *s-m*-nitrodibenzylidenehydrazine; *m*-hydroxybenzylideneaniline and ethereal benzylidenehydrazine yield m-*hydroxydibenzylidenehydrazine*, m. p. 162°; *p*-hydroxybenzylidenehydrazine and benzylideneaniline yield p-*hydroxydibenzylidenehydrazine*, m p. 239—240°.

C. S.

Additive Compounds of Aromatic Amines with Phenols. Josef Dollinger (*Monatsh.*, 1910, 31, 643—656. Compare Dyson, Trans., 1883, 43, 466; Hebebrand, Abstr., 1883, 61; Philip, Trans., 1903, 83, 814; Philip and Smith, *ibid.*, 1905, 87, 1735; Kremann, Abstr., 1906, ii, 266; Schreinemakers, Abstr., 1899, ii, 739; 1900, ii,

135). Additive compounds of quinol, α- and β-naphthol with benzidine, o-tolidine, and o-dianisidine can be prepared by mixing together hot saturated aqueous solutions of the components. They are all practically insoluble in water, are resolved into their components when boiled with dilute acids or alkalis, and with the exception of the compound of o-tolidine and α-naphthol, contain an equal number of hydroxyl and amino-groups. Most of the compounds give characteristic colorations with ferric chloride in aqueous solution.

The *additive compound* of benzidine and quinol,

$$C_{12}H_8(NH_2)_2,C_6H_4(OH)_2,$$

is best prepared from cold alcoholic solutions, and forms colourless, glistening, rhombic plates, m. p. 230° (decomp.). The *additive compound* of benzidine and β-naphthol, $C_{12}H_8(NH_2)_2,2C_{10}H_7\cdot OH$, forms colourless, iridescent plates, m. p. 177°.

The amount of quinol or β-naphthol in an aqueous solution can be determined by adding benzidine solution and weighing the product (97% of the theoretical). The *additive compound* of o-tolidine and quinol, $C_{12}H_6Me_2(NH_2)_2,C_6H_4(OH)_2$, can be prepared from ethereal solutions, and forms microscopic needles with a red colour. It has m. p. 158° after sintering at 140°. The *additive compound* of o-tolidine and α-naphthol, $C_{12}H_6Me_2(NH_2)_2,C_{10}H_7\cdot OH$, crystallises from dilute alcohol in reddish-coloured needles, m. p. 99°. The *additive compound* of o-tolidine and β-naphthol,

$$C_{12}H_6Me_2(NH_2)_2,2C_{10}H_7\cdot OH,$$

crystallises in glistening plates, m. p. 96°. The *additive compound* of dianisidine and quinol, $C_{12}H_6(OMe)_2(NH_2)_2,C_6H_4(OH)_2$, separates from a mixture of benzene and light petroleum as pale lilac-coloured crystals, m. p. 157° (decomp.). The *additive compound* of dianisidine and β-naphthol, $C_{12}H_6(OMe)_2(NH_2)_2,2C_{10}H_7\cdot OH$, crystallises in long, reddish-coloured needles, m. p. 96°. The *additive compound* of α-naphthylamine and α-naphthol, $C_{10}H_7\cdot NH_2,C_{10}H_7\cdot OH$, forms pale lilac-coloured needles, m. p. 60°, and is decomposed by boiling water. The *additive compound* of α-naphthylamine and β-naphthol crystallises in glistening, rose-coloured prisms, m. p. 73—74°. The *additive compound* of β-naphthylamine and β-naphthol forms colourless prisms, m. p. 125—126°.

The following pairs of substances do not form sparingly soluble additive compounds: β-Naphthylamine and α-naphthol, α-naphthylamine and quinol, benzidine and catechol, benzidine and resorcinol.

Some of the compounds appear to be acidic, others basic, and still others amphoteric. J. J. S.

Preparation of Condensation Products in the Anthracene Series. Badische Anilin- & Soda-Fabrik (D.R.-P. 222205).—The condensation of aminoanthraquinones with halogen ketones yielding products of the type A·NH·R·CO·R·NH·A has been previously described (this vol., i, 397); the reaction has now been extended to halogen diketones of the general type H·R·CO·CO·R·H (H = halogen), which yield with aminoanthraquinones a new series of compounds of the general formula A·NH·R·CO·CO·R·NH·A (A = anthraquinone residue).

4 : 4′-Dichlorobenzil (50 parts) is boiled with 1-aminoanthraquinone (100 parts) and sodium carbonate (20 parts) in nitrobenzene solution in the presence of cupric oxide until the reaction is complete, when, on cooling, the product separates in brown needles. The nitrobenzene can be replaced by other indifferent solvents, and the copper oxide by cuprous chloride. F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. Badische Anilin- & Soda-Fabrik (D.R.-P. 222206).—An extension of the type of condensation described in the previous patent; in the present case the general reaction is that by which one or more anthraquinone residues are connected through an imino-group with one or more phenanthraquinone radicles. Two mols. of a monohalogenated phenanthraquinone may condense with 2 mols. of a mono- or with 1 mol. of a di-aminoanthraquinone; similarly, one molecular proportion of a dihalogenated phenanthraquinone may combine with 2 mols. of a mono- or with 1 mol. of a di-aminoanthraquinone. These condensations take place in boiling nitrobenzene solution in the presence of copper oxide and sodium carbonate or acetate.

The *product* from monobromophenanthraquinone (3 parts) and 1-aminoanthraquinone (2·4 parts) is a violet-brown powder, insoluble in water, alkali, and dilute acids; it yields a violet-brown colour with concentrated sulphuric acid, and violet-brown with boric acid.

The *products* from monobromophenanthraquinone (4·8 parts) and 1 : 5-diaminoanthraquinone (2 parts), from dibromophenanthraquinone (5 parts) and 1-aminoanthraquinone (10 parts), and from dichlorophenanthraquinone (3 parts) and 1-aminoanthraquinone (3 parts) were also prepared.

The *dibromophenanthraquinone* was obtained by brominating phenanthraquinone in nitrobenzene solution at 100°, the product separating in crystalline form from the hot solution; it crystallises from acetic acid in long, glistening, golden needles, m. p. 388°.

Dichlorophenanthraquinone was analogously prepared in the presence of a halogen carrier; it crystallises from acetic acid in red needles, m. p. above 300°. F. M. G. M.

Tetramethylchrysaniline. Otto Fischer and Edg. Schmidt (*J. pr. chem.*, 1910, [ii], 82, 288—291).—The by-product obtained when 2-aminotetramethyl-4′ : 4″-diaminotriphenylmethane is oxidised by arsenic acid (Abstr., 1882, 833) is produced in larger quantity when a boiling solution of the leuco-base in xylene is treated with yellow mercuric oxide for twelve to fifteen hours. The suggestion that it is tetramethylchrysaniline, m. p. 229—230°, is proved to be correct. The *platinichloride* and *picrate* are described; the *nitrate*,

$$C_{23}H_{23}N_3,HNO_3,$$

is readily soluble in water. C. S.

Preparation of Azoxy-compounds. Fritz Reitzenstein (*J. pr. Chem.*, 1910, [ii]. 82, 252—270).—By the oxidation of certain aromatic mono- or di-amines by warm alkaline potassium ferricyanide, the author has obtained dyes which he regards as containing the azoxy-

group. The dyes are produced in satisfactory yield, are substantive in character, and generally can be diazotised and combined on the fibre. After the removal of the dye, chlorine is passed into the mother liquor, which can then be utilised again; thus dianisidine gives the *substance*,

$$OMe\cdot C_6H_3(NH_2)\cdot C_6H_3(OMe)\cdot N{-}N\cdot C_6H_3(OMe)\cdot C_6H_3(OMe)\cdot NH_2,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \diagdown\diagup \quad O$$

a dark red powder, which dyes wool and silk yellow. Aniline-*p*-sulphonic acid yields the *substance*, $SO_3Na\cdot C_6H_4\cdot N{-}N\cdot C_6H_4\cdot SO_3Na$ (with $\diagdown\diagup O$), and 2 : 6-dibromoaniline-4-sulphonic acid a corresponding *substance*, which is brick-red and dyes wool a more intense yellow than the preceding substance. Similar azoxy-dyes are produced from benzidinesulphonedisulphonic acid, benzidinesulphonic acid, naphthidine, *oo'*-diaminodiphenic acid, *p*-phenylenediaminesulphonic acid, atoxyl (*p*-aminophenylarsinic acid), diaminostilbenedisulphonic acid, diaminotolan, and 4 : 4'-diaminodiphenylmethane. C. S.

*endo*Bisazo-derivatives of Diphenylmethane. Henri Duval (*Bull. Soc. chim.*, 1910, [iv], 7, 852—861. Compare this vol., i, 559, 588).—The general character of this investigation has been discussed already, and most of the results recorded (Abstr., 1907, i, 663; 1908, i, 658, 706). The following new compounds are described: Bisazodiphenylmethane-4 : 4-dicarboxylic acid (*loc. cit.*) on reduction with zinc and hydrochloric acid furnishes *bishydrazodiphenylmethane*-4 : 4'-*dicarboxylic acid*, which is amorphous, but yields a *tetracetyl* derivative, crystallising in small, yellow needles. T. A. H.

Hemielastin. Elkan Wechsler (*Zeitsch. physiol. Chem.*, 1910, 67, 486—488).—Hemielastin (Horbaczewski, Abstr., 1883, 927) when hydrolysed with sulphuric acid gave the following numbers: ammonia, 0·4; humin nitrogen I, 3·1; humin nitrogen II, 4·9; histidine, 1·0; arginine, 4·2; monoamino-acids, 71·1; lysine, 3·4% of the total nitrogen.

These correspond with arginine, 1·86; histidine, 0·53; lysine, 2·48, and ammonia, 0·05% of the original hemielastin. J. J. S.

Guanylic Acid from the Pancreas. II. Hermann Steudel and P. Brigl (*Zeitsch. physiol. Chem.*, 1910, 68, 40—51. Compare Steudel, Abstr., 1908, i, 70).—Bang's β-guanylic acid is regarded as the acid potassium salt of guanylic acid. When repeatedly dissolved in water and precipitated, it becomes more soluble, owing to loss of potassium. The formula suggested is $C_{10}H_{13}O_8N_5PK$. A corresponding barium salt has been prepared. The amounts of guanine and pentose formed on hydrolysis agree with the amounts required for such a formula.

The pentose is shown to be arabinose.

Levene's guanosine could not be isolated (compare Abstr., 1909, i, 620). J. J. S.

Non-existence of Free or Combined Lecithins in the Yolk of Eggs. N. Alberto Barbieri (*Compt. rend.*, 1910, 151, 405—407. Compare Abstr., 1907, ii, 708).—From experiments on the yolks of 3000 eggs, the author has been unable to obtain any evidence for the existence of lecithins in this material. The fatty matters can be separated in a state of purity by the aid of neutral solvents. They contain nitrogenous substances, but these can be removed by simple dialysis, and chlorine was not detected amongst them. The fats yield on hydrolysis nothing but glycerol and fatty acids. The phosphorus, moreover, was entirely dialysable, and appears to be present chiefly in the form of phosphates.

The portion of the yolk soluble in ether, commonly described as consisting of lecithins, yielded only small quantities of a *platinichloride*, m. p. 215°, containing 4·43% of nitrogen. The same salt was obtained from those constituents of the yolk soluble in water and alcohol.

W. O. W.

Iodoproteins. Carl Neuberg (*Biochem. Zeitsch.*, 1910, 27, 261—270).—The author gives an account of some attempts to prepare iodine-containing hydrolysis products from iodoproteins, using iodogliadin, a derivative of wheat proteins. The method attempted was to partly hydrolyse the iodoprotein with sulphuric acid at about 37°, and then to digest the hydrolysis mixture with pancreatin, and to separate the iodo-derivative by fractionating out on copper. He also gives an account of similar experiments carried out by L. Scott on iodospongin. He draws attention to an error in the estimation of iodine in organic compounds when nitrate is employed in the destruction of organic matter, and water vapour is then distilled through the iodine-containing mixture in the presence of ferric chloride into potassium iodide solution. If nitrate is employed, nitric oxide, free chlorine (from the aqua regia), etc., interfere with the reaction.

S. B. S.

Gelatin and Tannin. Hans Trunkel (*Biochem. Zeitsch.*, 1910, 26, 458—492).—Gelatin and tannin can be precipitated quantitatively from solution. The same quantity of lime (1 gram) requires more tannin for precipitation (0·7 gram) when fresh than when the solution has stood for twenty-four hours (0·4 gram). By warming the solution, however, the original proportions are re-attained. By this means a calcium tannate stable to water is obtained. If excess of tannin is employed, a precipitate is obtained from which tannin can be continually extracted by water. Neither the water-stable nor water-unstable precipitates can be separated into the components by alcohol, which extracts only 97% alcohol. From the gelatin residue only 6% of a gelatinising residue can be obtained. By treatment of both tannates with water or alcohol, a small amount of gallic acid is formed. The author shows that the quantitative relationships between the gelatin and tannin in the precipitates formed in various dilutions follow approximately the exponential adsorption equation, and he concludes that chemical processes play but a subordinate part in the reaction between the two substances.

S. B. S.

Organic Chemistry.

Relation between the Specific Gravity and Optical Constants of Isomeric Organic Compounds. K. Heydrich (*Zeitsch. Kryst. Min.*, 1910, **48**, 243—305).—The crystallographic constants, specific gravity, and refractive indices were determined for the following: Methyl oxalate (monoclinic, $a:b:c=1{\cdot}0351:1:0{\cdot}3346$; $\beta=101°55'$. D 1·422. Refractive indices for D line [values for C and F lines are also given for each of the compounds], $\alpha=1{\cdot}4177$, $\beta=1{\cdot}4616$, $\gamma=1{\cdot}5521$). Succinic acid (monoclinic, $a:b:c=0{\cdot}5688:1:0{\cdot}6195$; $\beta=91°20'$. D 1·562—1·567. $\alpha=1{\cdot}4503$, $\beta=1{\cdot}5338$, $\gamma=1{\cdot}6100$). Catechol (monoclinic, $a:b:c=1{\cdot}6086:1:1{\cdot}0229$; $\beta=94°15'$. D 1·367—1·375. $\alpha=1{\cdot}595$, $\beta=1{\cdot}609$, $\gamma=1{\cdot}747$). Resorcinol (orthorhombic, $a:b:c=0{\cdot}9110:1:0{\cdot}549$. D 1·281—1·285. $\alpha=1{\cdot}5781$, $\beta=1{\cdot}6197$, $\gamma=1{\cdot}6273$). Quinol (ditrigonal-scalenohedral, $a:c=1:0{\cdot}6680$. D 1·328—1·332. $\omega=1{\cdot}6325$, $\epsilon=1{\cdot}6262$). 2 : 4-Dinitrotoluene (monoclinic, $a:b:c=0{\cdot}85930:1:0{\cdot}54076$; $\beta=94°18'$. D 1·518—1·521. $\alpha=1{\cdot}4423$, $\beta=1{\cdot}6619$, $\gamma=1{\cdot}7556$). 2 : 6-Dinitrotoluene (orthorhombic, $a:b:c=0{\cdot}5714:1:0{\cdot}5407$. D 1·538—1·540. $\alpha=1{\cdot}4788$, $\beta=1{\cdot}6694$, $\gamma=1{\cdot}7244$). Codeine (orthorhombic, $a:b:c=0{\cdot}9595:1:0{\cdot}8346$. D 1·309—1·315. $\alpha=1{\cdot}5428$, $\beta=1{\cdot}6355$, $\gamma=1{\cdot}6838$). *iso*Codeine (orthorhombic, $a:b:c=0{\cdot}6322:1:0{\cdot}5600$. D 1·361—1·367. $\alpha=1{\cdot}6070$, $\beta=1{\cdot}6422$, $\gamma=1{\cdot}6754$). ψ-Codeine (monoclinic, $a:b:c=2{\cdot}1942:1:1{\cdot}1036$; $\beta=108°14'$. D 1·288—1·290. $\alpha=1{\cdot}5743$, $\beta=1{\cdot}6021$, $\gamma=1{\cdot}6472$). Dicyanodiamide (monoclinic, $a:b:c=1{\cdot}1109:1:1{\cdot}4213$; $\beta=115°20'$. D 1·404—1·405. $\alpha=1{\cdot}5212$, $\beta=1{\cdot}5493$, $\gamma=1{\cdot}8471$). Melamine (monoclinic, $a:b:c=1{\cdot}4121:1:0{\cdot}9728$; $\beta=112°16'$. D 1·573. $\alpha=1{\cdot}4906$, $\beta=1{\cdot}7429$, $\gamma=1{\cdot}8721$). Potassium phenol-*o*-sulphonate (orthorhombic, $a:b:c=0{\cdot}7796:1:0{\cdot}4621$. D 1·733—1·734. $\alpha=1{\cdot}5265$, $\beta=1{\cdot}5677$, $\gamma=1{\cdot}6467$). Potassium phenol-*p*-sulphonate (orthorhombic, $a:b:c=0{\cdot}8790:1:1{\cdot}0017$. D 1·869—1·871. $\alpha=1{\cdot}5714$, $\beta=1{\cdot}6079$, $\gamma=1{\cdot}6942$).

In each of these isomeric groups an increase in sp. gr. is accompanied by an increase in the mean refractive index, the specific refractive power remaining practically the same. For the polymeric substances there is a much greater difference in the specific refractive power. L. J. S.

Hydrocarbons of the Wool Grease Oleins. I. Augustus H. Gill and Laurence R. Forrest (*J. Amer. Chem. Soc.*, 1910, **32**, 1071—1073).—The hydrocarbons obtained by the hydrolysis of distilled wool grease oleins were freed from cholesterol and fractionally distilled under 1 mm. pressure. Each fraction was crystallised from acetone, so that the material was finally divided into two series of ethylenic hydrocarbons ; the first, containing twelve terms soluble in acetone at 0°, ranged from heptadecylene to triacontylene, $C_{30}H_{60}$, whilst the insoluble series included nine members, from eicosylene,

$C_{20}H_{40}$, to nonacosylene, $C_{29}H_{58}$. The b. p., molecular weight, and iodine number of each fraction is given. W. O. W.

Historical Notes on *C*-Nitroso-compounds. EUGEN BAMBERGER (*Ber.*, 1910, **43**, 2353—2355. Compare Abstr., 1900, i, 500).—The following arguments are brought forward against Piloty's formula, $CMe_2{:}NO{\cdot}O{\cdot}NO$, for *ψ*-nitroles (*Ber.*, 1902, **35**, 3094 note).

(1) In all cases in which the hydrogen atom of the :NO·OH group of nitronic acid is replaced, the substituent becomes attached to carbon, for example, CHMe:NO·OH gives $CH_3{\cdot}CHBr{\cdot}NO_2$. (2) A nitrite of the type $CMe_2{:}NO{\cdot}O{\cdot}NO$, should be readily hydrolysed by water; *ψ*-nitroles are not. (3) Piloty's formula does not account in any way for the similarity between *ψ*-nitroles and true *C*-nitroso-compounds. J. J. S.

Action of Grignard's Reagents on Methylethylacraldehyde and the Preparation of Certain Diolefines. E. BJELOUSS (*Ber.*, 1910, **43**, 2330—2333).—A series of unsaturated secondary alcohols has been prepared by the action of magnesium ethyl, *iso*butyl, and *iso*amyl bromides on methylethylacraldehyde, and these alcohols have been transformed into diolefines containing conjugate double linkings by means of crystallised oxalic acid (Zelinsky, Abstr., 1902, i, 2).

δ-Methyl-Δ^γ-hepten ε-ol, CHEt:CMe·CHEt·OH, prepared from ethyl magnesium bromide and methylethylacraldehyde, is a colourless liquid with a strong odour, and has b. p. 103—104°/75 mm., D_4^{25} 0·8545, and n_D^{25} 1·44436. The *acetate*, $C_{10}H_{18}O_2$, has b. p. 113°/80 mm., and the *chloride*, $C_8H_{15}Cl$, b. p. 75—78°/53 mm. *δη-Dimethyl-Δ^γ-octen-ε-ol*, CHEt:CMe·CH(OH)·CH_2·$CHMe_2$, is a colourless, mobile liquid, b. p. 108—111°/40 mm. It has D_4^{25} 0·8444 and n_D^{25} 1·44503. The *acetate*, $C_{12}H_{22}O_2$, has b. p. 103—105°/20 mm., and the *chloride*, $C_{10}H_{19}Cl$, b. p. 76—79°/13 mm.

δθ-Dimethyl-Δ^γ-nonen-ε-ol, CHEt:CMe·CH(OH)·CH_2·CH_2·$CHMe_2$, has b. p. 110—112°/19 mm., D_4^{25} 0·8441, and n_D^{25} 1·44782. The *acetate*, $C_{13}H_{24}O_2$, has b. p. 122—125°/31 mm., and the *chloride*, $C_{11}H_{21}Cl$, b. p. 93—95°/18 mm., but evolves hydrogen chloride.

δ-Methyl-Δ^βδ-heptadiene, CHEt:CMe·CH:$CHMe_2$, is a colourless, mobile liquid, b. p. 131—132°. It has D_4^{25} 0·7551 and n_D^{25} 1·46211, and shows the usual exaltation.

βε-Dimethyl-Δ^ε-octadiene, CHEt:CMe·CH:CH·$CHMe_2$, has b. p. 165°, D_4^{25} 0·7754, and n_D^{25} 1·46136.

δθ-Dimethyl-Δ^ε-nonadiene, CHEt:CMe·CH:CH·CH_2·$CHMe_2$, has b. p. 185—189°, D_4^{25} 0·7779, and n_D^{25} 1·46189. J. J. S.

Preparation of Keto-alcohols. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 223207).—The condensation products of ketones and alcohols have previously been described (compare Abstr., 1905, i, 443, 732); when this reaction is carried out in the presence of alkali carbonates or hydroxides, it yields stable compounds of therapeutic value.

Methyl hydroxyethyl ketone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, a colourless,

odourless oil, miscible with water, alcohol, or ether in all proportions, b. p. 109—110°/30 mm., is prepared by treating acetone (3 parts) with 35% formaldehyde solution (1 part), slowly adding potassium carbonate, heating to 30—35°, and subsequently distilling the acidified solution in a vacuum. The *acetate* is a colourless oil, b. p. 96°/15 mm.

Methyl β-hydroxyisopropyl ketone, $CH_3{\cdot}CO{\cdot}CHMe{\cdot}CH_2{\cdot}OH$, a viscous, colourless oil, b. p. 90—95°/15 mm., is prepared in similar manner from methyl ethyl ketone. F. M. G. M.

The Fatty Acids. S. Fachini and G. Dorta (*Boll. chim. farm.*, 1910, **49**, 237—247).—The authors base a method for the separation of the solid fatty acids from the liquid and unsaturated fatty acids on the sparing solubility of the former in light petroleum of low boiling point (30—50°). Solutions of stearic, palmitic, and myristic acids in this solvent deposit the whole of the dissolved substance when cooled to −40° in alcohol and solid carbon dioxide. Lauric acid is somewhat more soluble. The separation of the above acids on cooling is also almost quantitative even when the solution contains liquid fatty acids. It cases where large amounts of the former are present in the mixture, it is advisable first to remove the greater part of them from the solution by moderate cooling, and subsequently to precipitate the rest at −40°. This procedure facilitates filtration. The method is conveniently employed for the separation of arachidic acid, which crystallises along with lignoceric acid when the fatty acids from arachis oil are treated in the manner indicated. R. V. S.

Mixed Anhydrides. Enos Ferrario (*Gazzetta*, 1910, **40**, ii, 95—100).—The method of preparation of benzoyl nitrate by the action of benzoyl chloride and silver nitrate (Francis, Trans., 1906, **89**, 1) may be applied to other organic nitrates, and also to nitrites.

Acetyl nitrite, $CH_3{\cdot}CO{\cdot}NO_2$, is prepared by the action of acetyl chloride on dry silver nitrite at −30° to −40°. It is finally distilled at 45° in carbon dioxide. For the purpose of estimating the nitrogen, the vapours are passed, mixed with carbon dioxide, over a heated copper spiral. Propionyl, butyryl, and benzoyl nitrites are prepared in similar manner. The nitrites obtained are identical with those prepared by Francesconi and Cialdea (Abstr., 1904, i, 707) by the action of nitrosyl chloride on silver salts. C. H. D.

Preparation of Derivatives of ββ-Dialkylpropionic Acids. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 222809).—It is found that the derivatives of ββ-dialkylpropionic acids of the general formula $CHR_1R_2{\cdot}CH_2{\cdot}CO_2H$ (where R_1 and R_2 are alkyl radicles) have with the exception of the methyl and ethyl derivatives valuable therapeutic properties, and are quite tasteless.

β-Ethylvaleryl chloride, b. p. 150—155°, prepared from β-ethylvaleric acid and pho-phorus pentachloride, yields when treated with ammonium hydroxide, *β-ethylvalerylamide*, m. p. 127·5°; the *carbamide*, m. p. 197°, is prepared in the usual manner.

Menthyl β-ethylvalerate, b. p. 155°/12 mm., is obtained by the action of the foregoing chloride on menthol in the presence of pyridine.

F. M. G. M.

Glucinum Lactate. G. Calcagni (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 229—233, 290—293).—From glucinum carbonate and lactic acid a salt of the composition $Gl_{13}(C_3H_5O_3)_6O_{10},19H_2O$ can be obtained, but it is not a chemical individual, for when its aqueous solution is fractionally precipitated with alcohol, precipitates of various compositions are obtained. Indirectly, however, indications were obtained of the existence of salts of compositions other than those studied by previous authors. The specific conductivity of a solution of lactic acid to which glucinum oxide is added at first decreases, then increases rapidly until one half the molecular quantity of the oxide is present. The conductivity then rises, but very slightly, reaching a maximum when the molecular quantity of glucinum oxide has been added. Further addition of glucinum oxide causes a decrease in conductivity. These results are obtained at all degrees of dilution, and analogous behaviour is observed when the depression of the freezing point of the solution is measured. Hence it is probable that in addition to the normal salt which has been supposed to exist, another is formed composed of equimolecular quantities of base and acid. Above the concentration corresponding with this salt, glucinum oxide dissolves in the solution without forming salts, and its presence modifies the nature of the solvent, so that the conductivity and freezing point of the solvent are lowered (compare Parsons, Robinson, and Fuller, Abstr., 1908, ii, 105). R. V. S.

Action of Sodium Alkyloxides on Ethyl Acetoacetate. Telemachos Komnenos (*Monatsh.*, 1910, 31, 687—693. Compare this vol., i, 361).—By the interaction of sodium methoxide and ethyl acetoacetate in methyl-alcoholic solution a practically quantitative yield of methyl acetoacetate can be obtained. When sodium amyloxide and amyl alcohol are used, amyl acetoacetate is obtained. The formation of ethyl acetoacetate from sodium ethoxide and methyl acetoacetate in ethyl-alcoholic solution also takes place readily.

In the distillation of methyl acetoacetate there is no formation of dehydracetic acid, but the latter is formed in large quantity when amyl acetoacetate is distilled, and the author recommends this as the best method of preparation. T. S. P.

Ozo-salts of Molybdenum. Arrigo Mazzucchelli and G. Zangrilli (*Gazzetta*, 1910, 40, ii, 49—73).—It has been shown (Abstr., 1907, i, 748) that molybdenum peroxide is capable of forming a complex oxalate. A number of similar salts have now been examined.

The addition of hydrogen peroxide to a solution of ammonium molybdenum oxalate yields a yellow solution, which deposits crystals of a *salt*, $(NH_4)_2C_2O_4,MoO_4$. When dilute solutions are used, a product containing a smaller proportion of oxygen is obtained. The *potassium* salt, $K_2C_2O_4,MoO_4$, forms yellow crystals. If finely powdered and shaken with hydrogen peroxide, crystals of a *salt*,

$$K_2C_2O_4,2MoO_4,3H_2O,$$

separate, and an orange *ammonium* salt of corresponding composition has been obtained. The sodium salt, precipitated by alcohol, has the

composition $Na_2C_2O_4,Mo_2O_7$, probably owing to hydrolysis. Potassium molybdoiodate yields only an amorphous product on oxidation, and ammonium molybdophosphate yields a product which does not contain active oxygen.

Potassium molybdoarsenate and hydrogen peroxide yield only a potassium ozomolybdate, $K_2MoO_5,3H_2O$, free from arsenic.

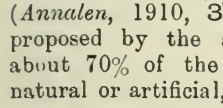
Cryoscopic measurements have been made, using solutions of various complex salts and acids of molybdenum, and adding successive quantities of hydrogen peroxide. The results show that the number of molecules present in the solution is not increased by such additions until the ratio $H_2O_2 : MoO_3$ is reached, and it appears that even a further quantity enters into combination. Such a salt as $(NH_4)_2C_2O_4,MoO_5$ may exist, the salt KVO_5 being already known.

The results are, however, complicated by a decomposition of the complex salts, and do not admit of any simple interpretation. Measurements with methyl molybdate have also been made as a means of determining the molecular complexity. C. H. D.

Synthesis of the αδ-Dimethyladipic Acids and Separation of the Racemic Acid into Optical Isomerides. William A. Noyes and L. P. Kyriakides (*J. Amer. Chem. Soc.*, 1910, 32, 1057—1061).—Lean has expressed the view that the carbon atoms in αβ-dialkylsuccinic acids and similar compounds are so united that optical isomerism is impossible (Trans., 1894, 65, 1001). That this is not the case is now shown by the resolution of αδ-dimethyladipic acid through the agency of its acid brucine salts. d-*αδ-Dimethyladipic acid*, m. p. 104—105°, has $[\alpha]_D^{28} + 31{\cdot}3°$ in 10% alcoholic solution. The *l*-form was obtained in an impure condition, having $[\alpha]_D - 23{\cdot}4°$. Attempts to resolve the meso-form were unsuccessful.

The preparation of αδ-dimethyladipic acid is considerably facilitated by substituting magnesium amalgam (Meunier, Abstr., 1904, i, 7) for sodium in the condensation of ethylene dibromide with ethyl malonate. W. O. W.

Camphenic (Camphenecamphoric) Acid. Ossian Aschan (*Annalen*, 1910, 375, 336—378).—Camphenic acid (the name is proposed by the author for camphenecamphoric acid) constitutes about 70% of the total oxidation products of camphene, whether natural or artificial, by alkaline potassium permanganate. In support of the annexed formula, the following facts are stated. Camphenic acid, $C_8H_{14}(CO_2H)_2$, m. p. 135·5—136·5°, is a saturated, monocyclic dicarboxylic acid which does not form an anhydride. It is a racemic compound, the active forms being optical antipodes, $[\alpha]_D \pm 1{\cdot}8°$, m. p. 143—144°; the *l*-form has been obtained by Wallach and Gutmann (Abstr., 1907, i, 1061), and the *d*-form by the author by the oxidation of a highly dextrorotatory camphene prepared from Grecian turpentine. Like camphoric acid, camphenic acid is converted by glacial acetic acid and hydrochloric acid, D 1·2, at 180° into an *isomeride* (trans-form ?), which, however, could not be isolated in a pure state (the separation of the two isomeric



acids has since been accomplished by Wallach). Camphenic acid (1 mol.) is treated with phosphorus pentachloride (2 mols.), and, after the cessation of the reaction, with bromine (rather more than 1 mol.) in the cold, whereby under conditions detailed by the author *α-bromocamphenic acid*, $C_8H_{15}Br(CO_2H)_2$, m. p. 190°, is obtained; only 1 atom of the halogen can be introduced smoothly. When bromocamphenic acid is heated with a solution of sodium carbonate on the water-bath for about fifteen minutes, it is partly converted into *dehydrocamphenic acid*, m. p. 155°, which receives the constitution $CO_2H\cdot CMe_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH:C\cdot CO_2H\end{matrix}$, because it is converted by nitric acid, D 1·252, on the water-bath into the *γ-lactone*,

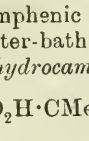
$$CO_2H\cdot CMe_2\cdot C(CO_2H)<\begin{matrix}CH_2\cdot CH_2\\ O--CO\end{matrix},$$

m. p. 254° (decomp.). The decomposition of the lactone by fusion with potassium hydroxide yields chiefly *iso*butyric acid, together with succinic and oxalic acids. The action of sodium carbonate on bromocamphenic acid also results in the formation of *hydroxycamphenic acid*,

$$CO_2H\cdot CMe_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot C(OH)\cdot CO_2H\end{matrix}',$$

m. p. 152°, which is stable to potassium permanganate, and is not affected by 40% sulphuric acid on the water-bath, thus proving that the hydroxyl group is not in the γ-position to a carboxyl group.

Whilst bringing forward the preceding constitution of camphenic acid with reserve, the author claims that much can be said in favour of the annexed constitution of camphene. Touching on the vexed question of the nature of camphene, the author is disinclined to accept Moycho and Zienkowski's suggestion of its dual character (Abstr., 1904, i, 438; 1905, i, 710), but leans to Semmler's view of its homogeneity. Nevertheless, in consequence of the large percentage of camphenic acid obtained by the oxidation of camphene, he rejects Wagner's "methylene" formula of camphene (which necessitates the assumption of the formation of several intermediate substances in order to explain the formation of camphenic acid) and proposes the "ethylene" formula given above. Certainly Wagner's claim that the camphenic acid is produced from the intermediately formed camphenylic acid must be wrong, because, as the author shows, the latter does not yield camphenic acid when oxidised by potassium permanganate. The formation of camphenic and camphenylic acids by the oxidation of camphene by alkaline potassium permanganate is easily explicable by the author's formula:



$$C_8H_{14}<\begin{matrix}CH\\ CH\end{matrix}\longrightarrow C_8H_{14}<\begin{matrix}CH\cdot OH\\ CH\cdot OH\end{matrix}\longrightarrow$$

$$C_8H_{14}<\begin{matrix}CO\longrightarrow C_8H_{14}(CO_2H)_2\\ CO\longrightarrow C_8H_{14}:C(OH)\cdot CO_2H\end{matrix}$$

the camphenylic acid being produced by a "benzylic acid" transformation in manner quite analogous to the formation of *β*-fenchocarboxylic acid from carbofenchenone. C. S.

New Formation of Carboxylic Acids of the Carbohydrates. Carl Neuberg (*Biochem. Zeitsch.*, 1910, 28, 355—358).—By the oxidation of dextrose with nitric acid (D 1·15) in addition to saccharic acid, a *carboxylic acid*, $CHO\cdot[CH\cdot OH]_4\cdot CO_2H$, identical or isomeric with glycuronic acid is formed. The *barium* salt, a colourless powder, and the free acid both strongly reduce Fehling's solution, give an intense colour reaction with naphtharesorcinol, and also show positive phloroglucinol and orcinol tests. Barium hydroxide produces a precipitate of an orange-coloured, flocculent basic salt. A furfuraldehyde distillation showed the conversion of 10 per cent. of the original dextrose into this form. E. F. A.

Carbithionic Acids. IV. Esters of Perthio acetic, -propionic, and -phenylacetic Acids. Josef Houben and Karl M. L. Schultze (*Ber.*, 1910, 43, 2481—2485. Compare Abstr., 1907, i, 382, 474).—*Methyl dithioacetate*, $CH_3\cdot CS\cdot SMe$, is prepared by the interaction of magnesium methyl iodide with carbon disulphide, treatment of the reaction mixture with ice, followed by the addition of ammonium chloride. The carbithionate is shaken with methyl sulphate, when a red oil separates, which is distilled with steam to destroy excess of methyl sulphate. The ester is a reddish-yellow oil, b. p. 80—81°/95 mm., 71°/70 mm., 142°/760 mm., D_4^{21} 1·096; it has a characteristic odour.

Methyl dithiopropionate, $CH_2Me\cdot CS\cdot SMe$, is a reddish-yellow oil, b. p. 92—93°/70 mm., 47°/11 mm., 159—160°/760 mm., D_4^{21} 1·047.

Methyl dithiophenylacetate, $CH_2Ph\cdot CS\cdot SMe$, is a reddish-yellow oil of characteristic odour, b. p. 149°/12 mm., 280°/760 mm. (decomp.), D_4^{24} 1·1389. E. F. A.

Hyposulphites. VIII. Aldehydesulphoxylates and Potassium Cyanide. Arthur Binz and Th. Marx (*Ber.*, 1910, 43, 2350—2352. Compare Binz, Abstr., 1909, ii, 229).—Neither rongalite nor potassium cyanide alone reduces indigocarmin in the cold, whereas a mixture of the two does. It is also shown that potassium cyanide accelerates the reducing power of rongalite towards indican, whereas it has no such effect on benzaldehydesulphoxylate.

The effects are probably catalytic. The reaction with indigocarmin is of interest, as it belongs to the group of reactions which take place only after the lapse of a certain time. J. J. S.

Dissociation Processes in the Sugar Group. II. Behaviour of Carbohydrates towards Alkali Hydroxides. John U. Nef (*Annalen*, 1910, 376, 1—119. Compare Abstr., 1905, i, 3; 1908, i, 5).—Twenty-four isomeric saccharinic acids with six carbon atoms are possible, namely, eight stereoisomeric *meta*saccharinic acids ($\alpha\gamma\delta\epsilon$-tetrahydroxyhexoic acids), $CO_2H\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$, derived from the sixteen aldohexoses; four stereoisomeric *iso*saccharinic acids ($\alpha\gamma\delta$-trihydroxy-α-hydroxymethylvaleric acids),

$$CO_2H\cdot C(OH)[CH_2(OH)]\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

derived from the eight β-ketohexoses; eight saccharinic acids ($\alpha\beta\gamma\delta$-tetrahydroxy-α-methylvaleric acids),

$$CO_2H\cdot CMe(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH;$$

and four *para*saccharinic acids ($\alpha\beta\gamma$-trihydroxy-$\alpha(\omega)$-hydroxyethyl-

butyric acids), $OH\cdot CH_2\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CH_2\cdot OH$. The eight saccharinic acids are formed from the eight 3-ketohexoses, but the *para*saccharinic acids are not obtained by the action of alkali hydroxides. Hence the number of possible C_6 saccharinic acids derived from the thirty-two different hexoses is theoretically twenty isomerides.

In the case of all carbohydrates, whether aldoses or ketoses, and irrespective of the number of carbon atoms, the salt formation with alkali hydroxides takes place at the carbon atom next the carbonyl group, $-CH(OH)\cdot CH(OM)\cdot CO-$. The methylene derivative,

$$-CH(OH)\cdot \hat{C}\cdot CO-,$$

in the absence of an oxidising agent undergoes rearrangement to glycide, $-CH\cdot CH\cdot CO-$ (with O), and this to *ortho*-osone, $-CH_2\cdot CO\cdot CO-$, from which by the benzilic acid tranformation saccharinic acids are formed. In the presence of an oxidising agent, oxygen is absorbed, and the 1 : 2-osone, $-CH(OH)\cdot CO\cdot CO-$, is formed. Enzymes act in a similar manner on the carbohydrates, but their barely basic nature does not bring about the transformation of the *ortho*-osones formed into saccharinic acids.

Similarly, four C_4 saccharinic acids are derived from the six isomeric tetroses, and ten C_5 saccharinic acids from the fifteen isomeric pentoses; in the following the two $\alpha\gamma$-dihydroxybutyric acids, the four $\alpha\gamma\delta$-trihydroxyvaleric acids, and α- and β-dextro*meta*saccharinic acids are described.

Hexoses decompose into a molecule each of diose and aldotetrose, or into 2 molecules of glyceraldehyde; the decomposition into formaldehyde and an aldopentose has never been observed. In nature, pentoses are never formed by the degradation of hexoses; hexoses are never built up from pentoses and formaldehyde. Pentoses form $\alpha\beta$-dienols, $OH\cdot CH{:}C(OH)\cdot(CH\cdot OH)_2\cdot CH_2\cdot OH$, which in the main give aldotetroses and hydroxymethylene; to some slight extent they form $\beta\gamma$-dienols, $OH\cdot CH_2\cdot C(OH){:}C(OH)\cdot CH(OH)\cdot CH_2\cdot OH$, which decompose into diose and glyceraldehyde. Dextroses exclusively form 2 : 3-dienols, and decompose into 2 molecules of diose; they never form hydroxymethylene and glyceraldehyde.

When hexoses or pentoses are treated with 8*N*-sodium hydroxide, only the C_6 or C_5 saccharinic acids of the corresponding series are formed, as the products of decomposition (hydroxymethylene, diose, glyceraldehyde, and aldotetrose) do not under these conditions undergo synthetic condensation to every possible hexose and pentose. Hydroxymethylene, however, forms the dienol, $CH(OH){:}CH(OH)$; this changes into glycolaldehyde, $CH_2(OH)\cdot CHO$, which condenses exclusively to tetrose, from which *d*- and *l*-$\alpha\gamma$-dihydroxybutyric acids are formed. It is not certain whether glyceraldehyde in the same manner gives exclusively *d*- and *l*-lactic acids.

When dilute sodium hydroxide is used, a mixture of every possible saccharinic acid with three, four, five, or six carbon atoms is obtained. This is the case when sparingly soluble metallic hydroxides, such as those of calcium and barium, are used. With 8*N*-sodium hydroxide the

pentoses give only six saccharinic acids, and hexoses only eight, namely, *d*- and *l*-lactic acids, *d* and *l*-αγ-dihydroxybutyric acids, and two *meta*- and two *iso*-saccharinic acids with six carbon atoms.

I. *l*-Arabinose and 8*N*-sodium hydroxide; 100 grams of sugar yield about 80 grams of non-volatile saccharinic acids, together with more or less of a dark reddish-brown, neutral resin soluble in water; this is chiefly formed from diose. After a lengthy process of separation, for the details of which the original must be consulted, d-*threo*-αγδ-*trihydroxyvaleric acid*, $CO_2H—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—CH_2\cdot OH$, and l-*erythro*-αγδ-*trihydroxyvaleric acid*, $CO_2H—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{H}{C}}—CH_2\cdot OH$, were isolated.

The *quinine* salt of the former crystallises in lustrous needles, m. p. 172°, $[\alpha]_D^{20}$ −103·3°. The *phenylhydrazide* forms voluminous, colourless needles, m. p. 110°, $[\alpha]_D$ +26·36°. The *brucine* salt separates in flat, lustrous prisms, $[\alpha]_D^{20}$ −18·77°; the *sodium* salt has $[\alpha]_D^{20}$ +23·76°.

d-*Threo*-αδ-*dihydroxyvalerolactone* is a colourless, mobile oil, $[\alpha]_D$ −36·5°; it is oxidised by dilute nitric acid to d-αγ-*dihydroxyglutaric acid*, m. p. 135°, $[\alpha]_D^{20}$ −2·6°; the *disodium* salt has $[\alpha]_D^{20}$ +22·25°.

l-*Erythrotrihydroxyvaleric acid* forms a *phenylhydrazide*, crystallising in colourless, concentrically-grouped, dense needles, m. p. 145—150°, $[\alpha]_D^{20}$ −8·93°. The *lactone* has $[\alpha]_D^{20}$ −45° to −55°.

dl-αγ-*Dihydroxybutyric acid* forms a *brucine* salt, m. p. 188° (decomp.), $[\alpha]_D^{20}$ −27·23°, and a *phenylhydrazide*, crystallising in needles, m. p. 130—131°; on oxidation, *dl*-malic acid is formed.

dl-βγ-*Dihydroxybutyric acid* yields a *phenylhydrazide*, m. p. 99°.

dl-αγ-*Dihydroxybutyric acid* can be resolved by means of brucine. The *brucine* salt of the *d*-isomeride had m. p. 188° (decomp.), $[\alpha]_D^{20}$ −20·1°, the free acid having $[\alpha]_D$ +20° (about); it yields *d*-malic acid on oxidation.

II. Glycollaldehyde and strong sodium hydroxide form a good deal of resin and traces of formic acid, the main product being *dl*-α-hydroxybutyrolactone. No trace of *dl*-lactic acid is formed.

III. *l*-Xylose with 8*N*-sodium hydroxide yields *l*-threo- and *d*-ethryotrihydroxyvaleric acids, the antipodes of those given by *l*-arabinose. The *quinine* salts of these two acids crystallise together, m. p. 165°, $[\alpha]_D$ −113·2°; that of the d-*erythro*-αγδ-*trihydroxyvaleric acid* forms lustrous needles, m. p. 172°, $[\alpha]_D$ −104°. The *phenylhydrazide* has m. p. 150°, $[\alpha]_D^{20}$ +9·38°.

l-*Threo*-αγδ-*trihydroxyvaleric acid* forms a *brucine* salt, crystallising in transparent, concentrically-grouped, flat prisms, m. p. 145—150°, $[\alpha]_D^{20}$ −34·07°; a *quinine* salt, separating in needles, m. p. 160—162°, $[\alpha]_D^{20}$ −119·45°; a *phenylhydrazide*, crystallising in colourless needles, m. p. 110—112°, $[\alpha]_D^{20}$ −25·43°, and a *lactone*, $[\alpha]_D^{20}$ +42·5°.

dl-*Threo*-αγδ-*trihydroxyvaleric acid phenylhydrazide*, prepared by the union of the antipodes, crystallises in needles, m. p. 128—130°, and is a true racemate.

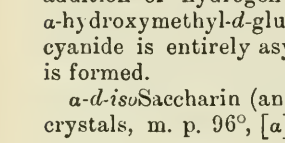
IV. *d*-Galactose with 8*N*-sodium hydroxide yields much less *dl*-lactic acid than dextrose, but, on the other hand, far more *dl*-$\alpha\gamma$-dihydroxybutyric acid.

The compound previously described (Abstr., 1908, i, 8) as giving brucine *dl-para*saccharinate, m. p. 193—194°, is in reality *dl*-α-hydroxybutyrolactone.

*meta*Saccharin and *para*saccharin are stereoisomerides, and correspond with the α- and β-*d*-galacto*meta*saccharinic acids. Accordingly, the four *para*saccharinic acids disappear from the literature.

[With Lucas]—The *lactone* of *α-hydroxymethyl*-d-*lyxonic acid*, prepared by the oxidation of an alkaline solution of galactose with air, forms crystals, m. p. 107—108°, $[\alpha]_D^{20}$ + 82·3°. The *brucine* salt crystallises in transparent, flat needles, m. p. 166°, $[\alpha]_D^{20}$ − 27·6°; the *quinine* salt has m. p. 162°, $[\alpha]_D^{20}$ − 107·5°; the *phenylhydrazide* has m. p. 162°, $[\alpha]_D^{20}$ − 11·06°. The lævulosecarboxylic acid, prepared by the addition of hydrogen cyanide to lævulose, has the formula of an α-hydroxymethyl-*d*-gluconic acid; apparently the addition of hydrogen cyanide is entirely asymmetric, as no isomeric lævulosecarboxylic acid is formed.

α-*d-iso*Saccharin (annexed formula) crystallises in heavy, measurable crystals, m. p. 96°, $[\alpha]_D^{20}$ + 61·9°. Characteristic are the calcium and quinine salts described by Kiliani (Abstr., 1904, i, 373). The *brucine* salt forms pointed needles, m. p. 164°; the *phenylhydrazide* forms needles, m. p. 120—122°, $[\alpha]_D^{20}$ + 19·6°.



α-*d*-Galacto*meta*saccharin (compare Kiliani, Abstr., 1905, i, 737) has m. p. 144°, $[\alpha]_D^{20}$ − 45·3°. The *brucine* salt forms transparent, hexagonal plates, m. p. 140°, $[\alpha]_D^{20}$ − 12·74°; the *strychnine* salt has decomp. 185—195°, $[\alpha]_D^{20}$ − 8·41°; the *barium* salt has $[\alpha]_D^{20}$ + 27·4°.

β-*d*-Galacto*meta*saccharin (Kiliani's *para*saccharin). The *strychnine* salt has m. p. 125—130°, $[\alpha]_D^{20}$ − 23°.

These α- and β-acids are related in the same manner as gluconic and mannonic acids, and are converted into one another on heating above 200°.

α-*d*-Galacto*meta*saccharonic acid (Kiliani, Abstr., 1885, 745) has m. p. 155°, $[\alpha]_D^{20}$ + 22·25°. The disodium salt has $[\alpha]_D$ + 19·11°. The β-isomeride (Kiliani, Abstr., 1904, i, 373, 975) forms a lactone, m. p. 159—160°, $[\alpha]_D^{20}$ − 98·05°; the disodium salt has $[\alpha]_D$ − 18·23°.

These isomeric *d*-$\alpha\gamma\delta$-trihydroxyadipic acids are readily converted when heated with acetic anhydride into *γ-hydroxymuconolactone*, $\begin{matrix}CH{:}CH\\ CO{-}{-}O\end{matrix}\!>\!C{:}CH{\cdot}CO_2H$, which crystallises in transparent, yellow plates, m. p. 228—230°.

V. Dextrose with 8*N*-sodium hydroxide yields a considerable quantity of *dl*-lactic acid, and about 25% of saccharins, mainly α- and β-*d*-dextro*meta*saccharin, with relatively little *iso*saccharin. There is also but little resin produced.

β-Dextro*meta*saccharin, m. p. 92°, $[\alpha]_D^{20}$ + 8·2°, forms a sparingly soluble *calcium* salt, $[\alpha]_D^{20}$ − 23·25°, a *brucine* salt crystallising in long, transparent, rectangular plates or needles, decomp. 130—150°,

$[\alpha]_D^{20}$ −33·14°, a *strychnine* salt, decomp. 180—190°, $[\alpha]_D^{20}$ −30·79°, a *quinine* salt, m. p. 150—155°, $[\alpha]_D^{20}$ −113·6°, and a *phenylhydrazide*, m. p. 124—126°, $[\alpha]_D^{20}$ −30·7°.

α-*Dextro*meta*saccharin*, m. p. 104°, $[\alpha]_D^{20}$ +25·28°, gives a soluble *calcium* salt, a *brucine* salt crystallising in transparent plates, m. p 150°, $[\alpha]_D^{20}$ −23·14°, a *strychnine* salt, m. p. 146°, $[\alpha]_D^{20}$ −19·5°, a *quinine* salt, colourless needles, m. p. 135—140°, $[\alpha]_D^{20}$ −100·9°; *phenylhydrazide* has m. p. 100—103°, and is optically inactive.

α-d-*Dextro*meta*saccharonic acid* has $[\alpha]_D^{20}$ −1·36°, yields a sparingly soluble characteristic *calcium* salt, and forms a *sodium* salt, $[\alpha]_D^{20}$ - 3·97°. The β-isomeride exists only as a *lactone* crystallising in prisms, m. p. 165°, $[\alpha]_D^{20}$ −4·73; the *sodium* salt has $[\alpha]_D^{20}$ −35·22°. Both these give γ-hydroxymuconic lactone when heated with acetic anhydride. Considerations based partly on the optical activity enable space formula to be assigned to all these acids.

VI. Formose synthesised from formaldehyde by means of lead hydroxide yields with 8*N*-sodium hydroxide a mixture of saccharins, in which C_5 and C_6 derivatives are present in equal quantities, indicating that formose consists about one half of hexoses and one half of pentoses.

VII. Any carbohydrate in weak alkaline solution is eventually converted into an equilibrium mixture in which one hundred and sixteen substances can take part, namely, the thirty-two aldoses with one to six carbons, the thirty-two corresponding methylenenols, the twenty-six ketoses with three to six carbons in an unbranched chain, and the twenty-six olefineols, that is, dienols. Methylenenols are continually polymerised to dienols; diose molecules give 2 : 3-dienols of tetroses. Methylenenols of aldotetroses cannot polymerise with one another or with C_3 molecules to octoses or heptoses, but they unite with hydroxymethylene or diosemethylenenol to αβ pentose- and βγ-hexose-dienols, from which the pentoses and hexoses are formed. The synthesis of sugar from formaldehyde never goes further than hexose. There is also no condensation of 6-hydroxymethylene molecules to inositol.

The fact that mannose, dextrose, and lævulose remain unchanged in aqueous solution proves that no trace of αβ-dienol,

$$OH\cdot CH{:}C(OH)\cdot[CH(OH)]_3\cdot CH_2\cdot OH,$$

is present. This enol and the isomeric aldoses are considered to be three entirely different substances having no tautomeric relation to one another.

In the formation of lævulic and formic acids on heating 2-ketohexoses with acids, 4-hydroxymethylfurfuraldehyde,

$$CHO\cdot C{:}CH\cdot CH{:}C\cdot CH_2\cdot OH,$$
$$\text{!}\_\_O\_\_\text{!}$$

is formed as an intermediate product, and the colour reactions with phenols are due to the formation of condensation products with this aldehyde. Mannose, dextrose, and galactose yield this aldehyde on heating with oxalic acid (Blanksma and Alberda van Ekenstein, Abstr., 1909, i, 228; this vol., i, 130, 461), due to a αβ-enolisation and conversion into β-ketohexose. Similarly, Fenton (Trans., 1901, **79**, 36, 807; 1909, **95**, 1334) has shown that 4-halogenmethylfurfuraldehyde is obtained from lævulose and more slowly from the aldohexoses on treatment with dry halogen hydride. Carbohydrates behave therefore very differently towards acids and alkalis. E. F. A.

Hexose Phosphoric Acid Ester. A. von Lebedeff (*Biochem. Zeitsch.*, 1910, 28, 213—229. Compare Abstr., 1909, i, 863).—The same hexose phosphoric acid ester is formed from dextrose and lævulose on fermentation with yeast juice. The compound with phenylhydrazine is considered to be the *phenylhydrazino-phosphoric acid* compound of a hexosazone, $C_{24}H_{31}O_7N_6P$, that is, $C_6H_8N_2,H_2PO_4\cdot C_6H_6(OH)_3(N_2HPh)_2$. It crystallises in canary-yellow bunches of needles of silky lustre, m. p. 148—150° (decomp.). When heated with hydrochloric acid, the corresponding *hexosonephosphoric acid* ester is formed; it yields an amorphous, sparingly soluble *lead* salt. When heated with potassium hydroxide, the hydrazinohexosazone yields dextrosazone and glyoxalosazone.

The hexose phosphoric ester forms a colourless, amorphous *phenylhydrazone*, also a p-*bromophenylhydrazone* crystallising in colourless needles, m. p. 128° (decomp.). The p-*bromophenylosazone* is yellow, m. p. 165°.

The ester is a compound of 1 mol. of carbohydrate and 1 mol. of phosphoric acid, which latter cannot be attached to the two terminal groups which react with phenylhydrazine. It is apparently different from the compound described by Young (Proc., 1907, 23, 65), and also differs from the glucophosphoric acid prepared by Neuberg and Pollak (this vol., i, 157, 610), which reacts with phenylhydrazine, forming glucosazone, and does not form a sparingly soluble phenylhydrazone.

E. F. A.

A Simple Method for the Preparation of Glucosamine Hydrochloride from Ovomucoid. Adolf Oswald (*Zeitsch. physiol. Chem.*, 1910, 68, 173—180).—By warming ovomucoid for about an hour with 3% hydrochloric acid, glucosamine hydrochloride is obtained from the products by simply concentrating on the water-bath. It then crystallises out. Ovomucoid contains glucosamine as such, not as a polymeric product.

W. D. H.

Derivatives of Lactose and of Maltose and Two New Glucosides. Emil Fischer and Hans Fischer (*Ber.*, 1910, 43, 2521—2536).—The method of synthesing disaccharides by the interaction of "β-bromoacetodextrose" and silver carbonate (Fischer and Delbrück, Abstr., 1909, i, 633) has been applied to "bromoacetolactose" and "bromoacetomaltose" with the expectation of obtaining tetrasaccharides. The hope has been partially fulfilled in the former case. A solution of "bromoacetolactose" in dry chloroform is shaken with freshly precipitated, dried silver carbonate, whereby a *substance*, $C_{24}H_{28}O_7(OAc)_{14}$, is obtained, which is probably the tetradeca-acetyl derivative of a tetrasaccharide; after purification by alcohol, it consists of a colourless, granular, indistinctly crystalline powder, which melts in boiling water. A sample, purified by shaking with dilute potassium hydroxide, has $[\alpha]_D^{21} + 20{\cdot}69°$ in chloroform. By hydrolysis in acetone with cold aqueous barium hydroxide, a substance is obtained, which, on account of its slight reducing action on Fehling's solution and the formation of a little phenyl-lactosazone with phenylhydrazine, is regarded as a mixture of about 25% of lactose (or of a substance which is easily converted into lactose) and a non-reducing carbo-

hydrate of high molecular weight, probably a tetrasaccharide; unfortunately, all attempts to obtain the latter in a pure state have been unsuccessful.

The interaction of "chloroacetomaltose" (or of the impure "bromoacetomaltose" described below) and freshly precipitated silver carbonate in moist ether yields *hepta-acetylmaltose*, $C_{26}H_{36}O_{18}$ m. p. 179—180° (corr.), which separates from alcohol in slender needles, strongly reduces warm Fehling's solution, and exhibits slight mutarotation, having $[\alpha]_D^{16}$ +72·62° to 76·66° in acetylene tetrachloride. From its method of formation it should be constituted similarly to hepta-acetylcellobiose (following abstract) and tetra-acetyldextrose, but it differs from these by its sparing solubility in dilute alkali.

The difficulty of obtaining crystallised "bromoacetomaltose" led the authors to examine the action of acetyl bromide on maltose. The direct interaction of the two substances, moderated by occasional cooling of the containing flask in a freezing mixture, yields a somewhat impure, amorphous bromohepta-acetylmaltose, which, however, can be used for the preceding and for the following experiment. *Hepta-acetylmenthylmaltoside*, $C_{36}H_{54}O_{18}$, m. p. 186° (corr.), obtained by shaking "bromoacetomaltose," dry silver carbonate, menthol, and ether for several hours, crystallises in needles, is odourless, does not reduce Fehling's solution, and has $[\alpha]_D^{19}$ +20·84° in *s*-tetrachloroethane. When its hot alcoholic solution is hydrolysed by boiling aqueous barium hydroxide, *menthylmaltoside*, $C_{22}H_{40}O_{11}$, m. p. 203° (corr.), $[\alpha]_D^{16}$ +14·23° in aqueous solution, is obtained, which separates from water in needles containing $2H_2O$, has an unpleasant taste, does not reduce Fehling's solution, and forms a *barium* salt, $(C_{22}H_{39}O_{11})_2Ba$.

The preparation of "bromoacetolactose" (bromohepta-acetyl-lactose) by Ditmar's method with acetyl bromide and dry lactose frequently miscarries from unknown causes. Therefore the authors employ the following very convenient method. A solution of octa-acetyl-lactose in acetic anhydride is treated with a saturated solution of hydrogen bromide in glacial acetic acid; after one hour and three-quarters at 15—20°, the mixture is poured into water at 0°, the precipitate is dissolved in chloroform, and is recovered by the addition of light petroleum to the washed and dried solution. By rapid crystallisation from warm alcohol the substance is obtained quite pure, and has m. p. 143—144° (corr.), and $[\alpha]_D^{22}$ +104·9° in chloroform. This method has also been employed in the preparation of "*β-iodoacetodextrose*," $C_{14}H_{19}O_9I$, m. p. 110—111° (corr.), $[\alpha]_D^{20}$ +231·9° in *s*-tetrachloroethane, from *α*- or *β*-penta-acetyldextrose in acetic anhydride, and hydrogen iodide in glacial acetic acid; it crystallises in colourless needles, and belongs probably to the *β*-series, since it is converted into tetra-acetyl-*β*-methyl glucoside by methyl alcohol and silver carbonate, in which case, therefore, its formation from *α*-penta-acetyldextrose must be accompanied by intramolecular change.

Hitherto synthetic glucosides of polyhydric alcohols have not been obtained in the crystalline state. This has now been achieved by the use of pure "bromoacetodextrose," which has the great advantage of forming easily crystallisable acetyl derivatives. *Tetra-acetyl-β-glycol-glucoside*, $C_{16}H_{24}O_{11}$, m. p. 101—103° (corr.), obtained by shaking

glycol, pure bromoacetodextrose, and dry silver carbonate for several hours, crystallises from water in stout prisms, does not reduce Fehling's solutions, has $[\alpha]_D^{16} - 26{\cdot}23°$ in aqueous solution, and is hydrolysed by aqueous barium hydroxide at the ordinary temperature, yielding *β-glycol-d-glucoside*, $C_8H_{16}O_7$, m. p. 137—138 (corr.), $[\alpha]_D^{16} - 30{\cdot}20°$ in aqueous solution, which can be obtained in stout crystals by the slow evaporation of its solution in alcohol–ethyl acetate, rapidly by inoculation when crystals have once been secured; it does not reduce Fehling's solution, and is rapidly hydrolysed by hot mineral acids and by emulsin, which indicates that the glucoside belongs to the *β*-series.

B. Helferich, by the preceding method, has obtained crystalline *d*-glucosides of benzyl alcohol, $[\alpha]_D^{20} - 55{\cdot}6°$, of *cyclo*hexanol, $[\alpha]_D^{20} - 41{\cdot}5°$, of geraniol, $[\alpha]_D^{27} - 37{\cdot}3°$, of cetyl alcohol, $[\alpha]_D^{18} - 22{\cdot}5°$, and of glycollic acid, $[\alpha]_D^{20} - 43{\cdot}8°$. C. S.

Derivatives of Cellobiose. Emil Fischer and Géza Zemplén (*Ber.*, 1910, 43, 2536—2543. Compare preceding abstract).—The experiments on cellobiose and their results are quite similar to those in the case of lactose. "*Bromoacetocellobiose*," $C_{12}H_{14}O_{10}BrAc_7$, is obtained by shaking octa-acetylcellobiose at the ordinary temperature with a solution of hydrogen bromide in glacial acetic acid saturated at 0°; it crystallises in needles, darkens at 180°, and melts and decomposes a few degrees higher, and has $[\alpha]_D^{20} + 96{\cdot}54°$ in chloroform. "*Iodoacetocellobiose*," $C_{12}H_{14}O_{10}IAc_7$, prepared in a similar manner (the isomeric octa-acetylcellobiose, m. p. 198°, may be used), forms needles, has m. p. 160—170° (decomp.), and $[\alpha]_D^{20} + 125{\cdot}6°$ in chloroform and 123·2° in *s*-tetrachloroethane. From either of these compounds, by boiling with water and calcium carbonate, or by shaking with silver carbonate in a moist solvent, most conveniently in acetone, *hepta-acetylcellobiose*, $C_{12}H_{15}O_{11}Ac_7$, m. p. 195—197°, is obtained, which crystallises from water in slender needles, has $[\alpha]_D^{20} + 19{\cdot}95°$ in chloroform, 19·58° in *s*-tetrachloroethane, and 18·85° after twenty minutes and 25·48° after twenty-six hours in methyl alcohol; it dissolves easily in cold, very dilute sodium hydroxide, and is not re-precipitated by acids. When "bromoacetocelloboise" is shaken with dry silver carbonate in dry chloroform for a few hours, a colourless, granular powder is ultimately obtained, which is a mixture consisting chiefly of the *tetradeca-acetyl* derivative of a tetrasaccharide, $C_{24}H_{28}O_{21}Ac_{14}$; by hydrolysis in acetone with cold saturated barium hydroxide it is converted into a substance, $[\alpha]_D^{20}$ 18·7° in water, which consists of a carbohydrate of high molecular weight mixed with about 30% of cellobiose, the amount of which is deduced from the reducing power of the substance and the weight of phenylcellobiosazone produced with phenylhydrazine. The carbohydrate has not been isolated in a pure state. C. S.

Destructive Distillation of Cellulose. Ernst Erdmann and C. Schaefer (*Ber.*, 1910, 43, 2398—2406).—The following substances have been obtained by subjecting cellulose to destructive distillation from a copper retort during two hours: (*a*) Gas containing carbon dioxide 0·2, heavy hydrocarbons 0·5, oxygen 0·9, carbon monoxide 65·5, methane 19, hydrogen 11·5, nitrogen 2·4 per cent.; (*b*) aqueous

liquid, about 40% of the original cellulose; this forms a reddish-brown liquid with a pungent odour, is strongly acidic, has reducing properties, and gives a deep purple coloration with ferric chloride; (*c*) brown mobile tar, 5% of the cellulose.

The following products have been isolated from the aqueous distillate after neutralising with sodium carbonate and subjecting to fractional distillation: Formaldehyde; furfuraldehyde; maltol (compare Brand, Abstr., 1894, i, 270; Kiliani and Balzen, Abstr., 1895, i, 80; Peratoner and Tamburello, Abstr., 1905, i, 807); ω-hydroxymethylfurfuraldehyde, the semioxazone of which is not molten at 260°, and γ-valerolactone. J. J. S.

Insoluble Lead Salts of Amino-acids. Phœbus A. Levene and Donald D. van Slyke (*J. Biol. Chem.*, 1910, 8, 285—286).—Both tyrosine and aspartic acid form lead salts which are nearly insoluble in water. The fact will probably be useful in the separation of these amino-acids from mixtures. W. D. H.

Synthesis of Polypeptides. Derivatives of *l*-Leucine. Emil Abderhalden and L. E. Weber (*Ber.*, 1910, 43, 2429—2435).—The complicated polypeptides afford materials for the study of the peptolytic enzymes. *d*-Alanyl-glycyl-glycine ($[\alpha]_D + 31°$) is hydrolysed by some enzymes to *d*-alanine and inactive glycyl-glycine as shown by a decrease in rotatory power. The pressed juice of cancer cells causes an increase in rotatory power, indicating hydrolysis to glycine and *d*-alanylglycine.

In order to have further test materials available, a number of new polypeptides have been prepared containing *l*-leucine and glycine. It is found that the introduction of each glycine group causes a large increase in lævorotation, an introduction of leucine working in the contrary direction.

Chloroacetyl-l-*leucine*, prepared by coupling the constituents in presence of sodium hydroxide, has m. p. 139—140° (corr.), $[\alpha]_D^{20} - 13{\cdot}1°$. By the action of ammonia at 37°, *glycyl*-l-*leucine* is formed, crystallising in plates which turn brown at 246° (corr.), m. p. 256° (corr., decomp.), $[\alpha]_D^{20} - 31°$. From the mother liquors an insoluble compound crystallising in plates, m. p. 223° (corr.), was obtained.

d-α-*Bromoisohexoyl-glycyl*-l-*leucine* crystallises in needles, m. p. 101° (corr.), $[\alpha]_D^{20} + 30{\cdot}4°$.

l-*Leucylglycyl-leucine*,

$CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO_2H$,

is obtained as a granular powder, m. p. 256—266° (decomp.), $[\alpha]_D^{20} + 6{\cdot}0°$.

Chloroacetyl-l-*leucyl-glycyl*-l-*leucine* is obtained in small, hygroscopic needles, which soften at 70°, $[\alpha]_D^{20} - 9{\cdot}1°$.

Glycyl-l-*leucyl-glycyl*-l-*leucine* is a granular powder which becomes brown at 240°, m. p. 256—257° (corr.), $[\alpha]_D^{20} - 51{\cdot}0°$.

l-*Leucyl-glycyl*-l-*leucyl-glycyl*-l-*leucine* is a crystalline powder which becomes brown at 210°, m. p. 256—266° (corr., decomp.), $[\alpha]_D^{20} - 14{\cdot}5°$.

E. F. A.

Synthesis of Polypeptides. Derivatives of *iso*Leucine. III. Emil Abderhalden and Paul Hirsch (*Ber.*, 1910, **43**, 2435—2441. Compare Abstr., 1909, i, 769).—*l*-Leucyl-*d*-*iso*leucine has $[\alpha]_D^{20}$ +18·13°, and shows no biuret reaction.

l-*Leucyl*-d-iso*leucine anhydride*,

$$CHMe_2\cdot CH_2\cdot CH\begin{matrix}NH\cdot CO\\ CO\cdot NH\end{matrix}CH\cdot CHMeEt,$$

forms slender needles, m. p. 291° (corr.), $[\alpha]_D^{20}$ −35·76°.

d-α-*Bromopropionyl*-l-*leucyl*-d-iso*leucine*, prepared by coupling the constituents in the usual manner, sinters at 153°, m. p. 164° (corr.), $[\alpha]_D^{20}$ −23·37°.

d-*Alanyl*-l-*leucyl*-d-iso*leucine* forms minute needles, sinters at 231°, and has m. p. 245° (corr., decomp.). In *N*-hydrochloric acid it has $[\alpha]_D^{20}$ −24·89; in *N*-sodium hydroxide, $[\alpha]_D^{20}$ −45·72°; in water, $[\alpha]_D^{20}$ −9·12°. The tripeptide gives a violet biuret reaction and forms a *copper* salt.

Chloroacetyl-d-*alanyl*-l-*leucyl*-d-iso*leucine* separates in tiny needles, which sinter at 189°, m. p. 197°, $[\alpha]_D^{20}$ −54·83°.

Glycyl-d-*alanyl*-l-*leucyl*-d-iso*leucine*, obtained by the action of ammonia on the previous compound, sinters at 231°, m. p. 251° (corr., decomp.). In *N*-hydrochloric acid, it has $[\alpha]_D^{20}$ −80·59°; in *N*-sodium hydroxide, $[\alpha]_D^{20}$ −78·44°. It shows a pronounced biuret coloration, and forms a *copper* salt. E. F. A.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVI. Action of Ammonia and Amines on Thiocarbonates. Marcel Delépine and Paul Schving (*Bull. Soc. chim.*, 1910, [iv], 7, 894—902).—The action of ammonia and of primary and secondary amines on thiocarbonates of the following five types has been studied: $SR_1\cdot CS\cdot SR_2$, $OR_1\cdot CS\cdot SR_2$, $OR_1\cdot CS\cdot OR_2$, $SR_1\cdot CO\cdot SR_2$, $OR_1\cdot CO\cdot SR_2$.

With ammonia at atmospheric temperatures there are formed in the course of three or four days, urethanes of the following types respectively for the compounds indicated above: $SR_1\cdot CS\cdot NH_2$, $OR_1\cdot CS\cdot NH_2$, $OR_1\cdot CS\cdot NH_2$, $SR_1\cdot CO\cdot NH_2$, $OR_1\cdot CO\cdot NH_2$. In the cases of types two and three some ammonium thiosulphate is formed, not as Salomon supposed (this Journ., 1873, 617), due to the presence of impurities, but to atmospheric oxidation (compare Husemann, *Annalen*, 1862, 123, 68; 126, 297, and Conrad and Salomon, this Journ, 1875, 753). With ammonia at 100° the three first types yield ammonium thiocyanate, and types four and five, carbamide.

Primary amines react in a manner strictly analogous to ammonia, furnishing at atmospheric temperature, and in the course of several days, the corresponding urethanes, thus: $SR_1\cdot CS\cdot NHR_3$, $OR_1\cdot CS\cdot NHR_3$ $OR_1\cdot CS\cdot NHR_3$, $SR_1\cdot CO\cdot NHR_3$, $OR_1\cdot CO\cdot NHR_3$. With excess of the primary amine at 100° the corresponding dialkylcarbamides are formed, the action taking place very slowly in the case of type two, where the ester used was SMe·CS·OMe, and the amine, ethylamine, but similar results were obtained with aniline.

With secondary amines the action tends to remain at the urethane stage even with excess of the amine at 100—120°.

Dimethyl trithiocarbonate, $CS(SMe)_2$, D_4^0 1·2820, D_4^{21} 1·2630, b. p. 225°, is an orange-yellow, highly refractive oil of peculiar odour (compare Cahours, *Ann. Chim. Phys.*, 1847, [iii], **19**, 158).

Ethyl diethylthioncarbamate, $NEt_2{\cdot}CS{\cdot}OEt$, b. p. 224°, is a colourless liquid. *Methyl piperidylthioncarbamate*, $C_5H_{10}N{\cdot}CS{\cdot}OMe$, m. p. 23°, b. p. 120—122°/16 mm., obtained by the action of piperidine on methyl thiothioncarbonate, $OMe{\cdot}CS{\cdot}SMe$, is crystalline, possesses a mint-like odour, evolves sulphuric acid vapours at 100°, and phosphoresces (compare this vol., i, 295). *Propyl thioncarbamate*,

$$OPr^{\alpha}{\cdot}CS{\cdot}NH_2,$$

m. p. 35°, formed by the action of ammonia on the ester,

$$OPr^{\alpha}{\cdot}CS{\cdot}SMe,$$

is crystalline. *Methyl dimethylthiocarbamate*, $NMe_2{\cdot}CO{\cdot}SMe$, D_4^0 1·1098, D_4^{22} 1·0895, b. p. 180°, obtained by the action of dimethylamine on methyl dithiocarbonate, $CO(SMe)_2$, is a colourless liquid with a fungoid odour. T. A. H.

Colour of Vanadium Thiocyanate. C. Bongiovanni (*Boll. chim. farm.*, 1910, **49**, 467—468).—When a solution of vanadium sulphate is treated with barium thiocyanate, a green liquid is obtained, and it has consequently been supposed that vanadium thiocyanate is green, in contradistinction to the vanadithiocyanates of the alkali metals, which are violet. The author advances reasons for the view that the green colour is a result of hydrolytic processes due to the presence of sulphates. Vanadium chloride and thiocyanic acid give an intense reddish-violet coloration, which becomes green on addition of sulphates, or of ammonium oxalate or acetate. These substances also decolorise the red solution obtained when a ferric salt is treated with a thiocyanate. It appears probable, therefore, that vanadium thiocyanate has a colour similar to that of the vanadithiocyanates. R. V. S.

New Method for the Preparation of Aliphatic Nitriles. Alexander E. Arbusoff (*Ber.*, 1910, **43**, 2296—2300).—Good yields of aliphatic nitriles can be obtained by heating the phenylhydrazones of some of the higher aliphatic aldehydes with metallic salts, such as cuprous chloride, platinous chloride, or zinc chloride. The reaction proceeds according to the equation:

$$C_5H_{10}{:}N{\cdot}NHPh = NH_2Ph + C_5H_9N.$$

The following nitriles have been prepared by heating the phenylhydrazone with a small amount of cuprous chloride (0·2 gram) at 180—200°, and subjecting the products to fractional distillation under reduced pressure: *iso*valeronitrile, 56%; *iso*butyronitrile, 37%; heptonitrile, 60% yield. J. J. S.

The Supposed Lead Ferricyanide is a Lead Ferricyanide-nitrate. Erich Müller and Otto Diefenthäler (*Ber.*, 1910, **43**, 2321—2323).—The dark red precipitate which is obtained by the interaction of solutions of lead nitrate and potassium ferricyanide is

not lead ferricyanide, as has hitherto been supposed, but lead ferricyanide-nitrate, $Pb_2[Fe(CN)_6]NO_3,5H_2O$.

It is suggested that the constitution is either $NO_3{\cdot}Pb{\cdot}Pb{:}FeC_6N_6$ or $Pb{:}Fe(C_6N_6){\cdot}Pb{\cdot}NO_3$, and the fact that the dark red crystals give a light greenish-yellow solution indicates that there may be an equilibrium between these two forms. T. S. P.

The Action of Hydrogen Aurichloride on Aqueous Solutions of Potassium Ferrocyanide. Ernst Beutel (*Monatsh.*, 1910, **31**, 871—881).—The reaction between hydrogen aurichloride and potassium ferrocyanide in aqueous solution depends on the relative proportions of the two reagents. In the first experiments a solution containing 4·6400 grams of hydrogen aurichloride and 8·5356 grams of potassium ferrocyanide per litre was used, this corresponding with 4 mols. of the former to 3 mols. of the latter compound. The solution, when made, rapidly became emerald-green, changing to deep blue in the course of twelve hours. At the end of eight days, during which the solution was exposed to sunlight in a sealed flask, a deep blue precipitate had deposited, leaving a colourless, supernatant liquid. The precipitate consisted of pure ferric ferrocyanide, and the supernatant liquid contained the aurocyanide, auricyanide, and aurichlorocyanide of potassium, potassium chloride, and hydrochloric acid. The quantitative results were in accordance with the equation: $28HAuCl_4 + 21K_4FeC_6N_6 = 8KAuC_4N_4 + 6KAuC_2N_2 + 14KAuCl_2C_2N_2 + 56KCl + 28HCl + 3Fe_4(FeC_6N_6)_3$. The reaction products could not, for the most part, be isolated from the solution, owing to the fact that on concentration the complex cyanides are decomposed by the hydrochloric acid with the formation of aurous cyanide. Potassium auricyanide was isolated, since it resists the action of the mineral acid to a great extent.

The supernatant liquid already mentioned will enter into further reaction with the two reagents. With hydrogen aurichloride, it turns sulphur-yellow, and aurous cyanide is precipitated after a short time. With potassium ferrocyanide, it turns green, and then gives a bluish-green precipitate of a mixture of ferric hydroxide and ferric ferrocyanide. On long exposure to the light, the precipitate becomes pure ferric hydroxide only. Exact equations could not be given for these reactions.

In the next series of experiments, approximately equimolecular solutions of the two reagents (10 grams of hydrogen aurichloride per litre $= A$; 10 grams of potassium ferrocyanide per litre $= B$) were mixed in varying proportions. With mixtures varying from $3A : B$ to $25A : B$, the chief reaction is the precipitation of aurous cyanide. With $A : B$, the solution gradually changes from a light green to a dark brown, and retains the latter colour for a long time in diffused daylight or in the dark, no precipitate being formed. On exposure to sunlight, the colour changes to emerald-green, then dark blue, and finally disappears, a dark blue precipitate being deposited. With $A : 2B$ an emerald-green solution is obtained immediately, and the solution gradually, quicker on warming, deposits blue ferric ferrocyanide, leaving a yellow supernatant liquid containing the excess of potassium ferrocyanide. Similar results are obtained with $A : 3B$ and

$A:5B$, but the blue precipitate takes much longer to form. With $A:10B$ and $A:25B$, green solutions are obtained, which only on long keeping in sunlight deposit small quantities of ferric hydroxide, leaving a yellow solution containing ferro- and ferri-cyanide.

Potassium ferricyanide behaves similarly to potassium ferrocyanide towards hydrogen aurichloride, but a quantitative investigation is still wanting. T. S. P.

Action of Aqueous Solutions of Potassium Ferrocyanide on Aurous Cyanide and Gold Hydroxide. Ernst Beutel (*Monatsh.*, 1910, **31**, 883—886).—When aurous cyanide is heated with a solution of potassium ferrocyanide, oxygen being passed through the solution during the heating, it dissolves with the formation of potassium aurocyanide, ferric hydroxide being precipitated according to the equation:

$$8AuCN + 2K_4FeC_6N_6 + 5H_2O + O = 8KAuC_2N_2 + 2Fe(OH)_3 + 4HCN.$$

Gold hydroxide dissolves in a solution of potassium ferrocyanide with the formation of potassium gold cyanide and the precipitation of ferric hydroxide. The reaction takes place at room temperature, but much quicker on warming. Quantitative experiments were not made, and the particular potassium gold cyanide formed is not stated.

Fulminating gold also dissolves in solutions of potassium ferrocyanide. The solution first becomes emerald-green, and hydrogen cyanide is evolved. A green precipitate is then produced, which finally changes to brown ferric hydroxide. Potassium gold cyanide remains in solution. T. S. P.

Solubility of Finely-divided Gold in Solutions of Potassium Ferrocyanide. Ernst Beutel (*Monatsh.*, 1910, **31**, 887—890).—Finely-divided gold will dissolve completely in solutions of potassium ferrocyanide at room temperature. The rate of solution is very slow, even at the boiling point. Potassium aurocyanide is formed, and the resulting ferro-ions are oxidised by the oxygen of the air, giving ferric hydroxide. The solution formed is alkaline. The reaction probably takes place according to the equation:

$$3Au + K_4FeC_6N_6 + 2H_2O + O_2 = 3KAuC_2N_2 + Fe(OH)_3 + KOH.$$

T. S. P.

Estimation of Diazo-alkyls. E. K. Marshall and Salomon F. Acree (*Ber.*, 1910, **43**, 2323—2330).—Wegscheider and Gehringer's statement (Abstr., 1903, i, 685), that the yield of ester obtained by the action of an ethereal solution of diazomethane on an acid is greater than would be expected from the concentration of the diazomethane solution as determined by titration with iodine (Pechmann, Abstr., 1894, i, 438), is confirmed. The same solution of diazomethane does not give concordant results when titrated by the iodine method.

For estimating the concentration of a diazomethane solution, the authors recommend the use of an excess of *m*- or *p*-nitrobenzoic acid in ethereal solution and titrating the excess of acid by means of standard alkali after diluting with water, or actually isolating the methyl ester by extraction with chloroform after shaking with water

and sodium hydrogen carbonate solution. The results are correct to within 2—3%. Low results are obtained in the presence of alcohol.

Diazoethane can be estimated in a similar manner. J. J. S.

The Alkyl and Aryl Compounds of Tin. Paul Pfeiffer [with R. Lehnhardt, H. Luftensteiner, Rudolf Prade, K. Schnurmann, and P. Truskier] (*Zeitsch. anorg. Chem.*, 1910, **68**, 102—122).—A number of organic derivatives of quadrivalent tin have been described, as a preliminary to the study of their molecular compounds for comparison with those of cobalt, chromium, and platinum.

In the preparation of methylstannic acid from methyl iodide and an aqueous-alcoholic solution of potassium stannate, carbon dioxide precipitates small, glistening crystals of *potassium methylstannicarbonate*, $SnMeO{\cdot}O{\cdot}CO_2K,H_2O$, an aqueous solution of which decomposes on boiling, yielding methylstannic acid.

Dimethylstannic halides are best prepared by heating tin with methyl iodide, converting the product into oxide by means of ammonia, and then into the chloride by means of hydrogen chloride. After crystallising from light petroleum to remove the monomethyl compound, the chloride is converted into the oxide and then into the required salts. The chloride, bromide, and iodide have m. p.'s 108°, 78°, and 43° respectively. *Dimethylstannic oxalate*, $SnMe_2C_2O_4$, forms a white precipitate, soluble in a solution of potassium oxalate. *Dimethylstannic sulphide* is a white precipitate, soluble in ammonium sulphide.

Dipropylstannic bromide, $SnPr_2Br_2$, forms large, colourless needles, m. p. 49°.

Dibutylstannic oxide, $SnO(C_4H_9)_2$, when prepared by the action of aqueous-alcoholic ammonia on the pure chloride, forms an insoluble, amorphous powder. The *chloride*, $Sn(C_4H_9)_2Cl_2$, is sparingly soluble in water and has m. p. 43°; the *bromide* has m. p. 20°.

Di*iso*amylstannic oxide yields a basic chloride, m. p. 145°, on treatment with hydrochloric acid followed by pyridine.

Tribenzylstannic chloride, $Sn(C_7H_7)_3Cl$ (Abstr., 1904, i, 232), melts at 142—144° after crystallisation from glacial acetic acid. Pyridine is without action on it. Sodium carbonate solution converts it into *tribenzylstannic hydroxide*, $Sn(C_7H_7)_3{\cdot}OH$, crystallising in colourless, rhombic tablets, m. p. 117—121°. It is insoluble in water, but soluble in many organic solvents. Acetyl or benzoyl chloride converts it into the chloride, and not into the acetate or benzoate, in this respect resembling the reaction with the corresponding silicon compounds (Robison and Kipping, Trans., 1908, **93**, 439). *Tribenzylstannic bromide* has m. p. 125—128°.

Tin tetrapropyl boils at 228°.

*Tin tetra-*p*-tolyl*, $Sn(C_6H_4Me)_4$, prepared by the action of magnesium, followed by stannic bromide, on *p*-bromotoluene, forms colourless, glistening needles, m. p. 230°. C. H. D.

Constituents of Coal Tar. VI. *iso*Propylbenzene (Cumene). Gustav Schultz (*Ber.*, 1910, **43**, 2517—2521. Compare this vol., i, 897).—[With A. Székely.]—The viscous, brown, crude acids

obtained by the sulphonation of the "mesitylene" fraction are decomposed by superheated steam, and the resulting hydrocarbons are repeatedly distilled, whereby a fraction, b. p. 150—161°, is obtained, from which cumene is isolated as follows. The fraction is nitrated, and the portion of the product which is easily volatile with steam is fractionally distilled; the chief portion, b p. 145—150°/30—32 mm., is redistilled, whereby a *nitro*-compound, $C_9H_{11}O_2N$, b. p. 240—245° or 130—133°/15—16 mm., is obtained, which is proved to contain nitrocumene by the following experiments. A portion is reduced by tin and hydrochloric acid, and the amine, b. p. 223—230°, is separated into three fractions, b. p. 223—225°, 225—228°, and 228—230°. The first faction is treated with the calculated quantity of oxalic acid, whereby the oxalates of *p*-cumidine and of *o*-cumidine are obtained; also a portion of the fraction, after being acetylated, yields aceto-*p*-cumidide and acetomesidide. Another portion of the nitro-compound is boiled with 3 parts of nitric acid, D 1·48, and 4·5 parts of water for six days, whereby *p*-nitrobenzoic acid is produced. A third portion yields by further nitration trinitromesitylene and other trinitro-compounds which have not been separated.

A portion, b. p. 150—155°, of the original oil is sulphonated by concentrated and fuming sulphuric acids, and from the products *o-iso*propylbenzenesulphonic acid has been isolated in the form of the sulphonamide, m. p. 96—98°. C. S.

3 : 3′-Dimethyldiphenyleneiodonium Hydroxide and Some of Its Salts. Luigi Mascarelli and T. Cerasoli (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 308—311. Compare Abstr., 1909, i, 907).—3 : 3′-Dimethyldiphenyleneiodonium iodide is obtained in small quantity by diazotising 6 : 6′-diamino-3 : 3′-dimethyldiphenyl and treating the product with potassium iodide. It yields the above *hydroxide* when treated with moist silver oxide. The *iodide* is a yellow powder, m. p. 246°. The *bromide* is a white powder becoming yellow, m. p. 281°. The *chloride* forms a white, microcrystalline powder, becoming brown, m. p. 290°. The *oxalate*, $\left(\begin{matrix}C_6H_3Me\\ I\\ C_6H_3Me\end{matrix}\!\!>\!I\right)_2C_2O_4$, forms colourless, acicular crystals, m. p. 228°. R. V. S.

Esters of Benzenesulphon-nitroanilides. Stanislaus Opolski (*Bull. Acad. Sci. Cracow*, 1910, 126—128. Compare Abstr., 1907, i, 908).—To complete the proof that intramolecular change occurs when the three almost colourless benzenesulphon-nitroanilides are converted into their highly coloured salts, it is necessary to isolate the coloured *aci*-esters in addition to the ordinary colourless esters. All attempts to isolate the former, however, have been unsuccessful. By the action of alkyl iodides on the silver salts, the colourless esters are obtained, together with a red oil, from which a crystalline substance cannot be isolated.

The trinitro-compound obtained by the nitration of benzenesulphon-*o*-nitroanilide or of benzenesulphon-*p*-nitroanilide must be benzene-

sulphonpicramide, but attempts to prepare it by the condensation of picramide and benzenesulphonyl chloride, or of picryl chloride and benzenesulphonamide, have been unsuccessful.

Benzenesulphon-o-nitroethylanilide, $NO_2 \cdot C_6H_4 \cdot NEt \cdot SO_2Ph$, m. p. 103—104°, and *benzenesulphonbenzyl-o-nitroanilide*,

$$NO_2 \cdot C_6H_4 \cdot N(CH_2Ph) \cdot SO_2Ph,$$

m. p. 148—149°, unlike the colourless methyl esters, have a distinct yellow tinge. *Benzenesulphonmethylpicramide*,

$$(NO_2)_3 \cdot C_6H_2 \cdot NMe \cdot SO_2Ph,$$

m. p. 181—182°, forms colourless crystals. C. S.

Preparation of Aromatic Alkyl Ethers. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 224388).—An extension of the work described in the chief patent (Abstr., 1908, i, 263) to the reaction between substances containing one or more phenolic hydroxyl groups and the nitroso-compounds of acid amides of the general formula $-NR \cdot NO$, where R = alkyl.

The *product* obtained from β-naphthol and nitrosobenzenesulphonethylamide has m. p. 60°. When morphine suspended in methyl alcohol is treated with *p*-toluenesulphononitrosomethylamide in the presence of an alkaline hydroxide, a crystalline *compound*, m. p. 60°, is obtained.

Nitroso-β-naphthalenesulphonomethylamide has m. p. 85°. The morphine and β-naphthol in the foregoing condensations can be replaced by other phenols, cresols, or dihydroxybenzenes. F. M. G. M.

Acenaphthene. Franz Sachs and Gerhardt Mosebach (*Ber.*, 1910. 43, 2473—2475).—4-Aminoacenaphthene yields the 4-halogen derivatives of acenaphthene when treated according to the Sandmeyer reaction. An intense dark green coloration is produced on diazotisation. 4-Chloroacenaphthene forms slender needles, m. p. 62·5—63°; 4-bromoacenaphthene has m. p. 51·5° (compare Graebe, Abstr., 1903, i, 408); 4-*iodoacenaphthene* crystallises in rosettes of colourless, slender needles, m. p. 63—63·5° [compare Crompton, Proc. 1910, 26, 226]. E. F. A.

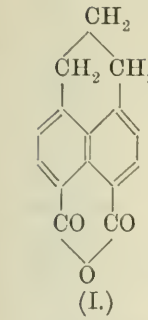
Structure of Pyrene. Egon Langstein (*Monatsh.*, 1910, 31, 861—870. Compare Goldschmiedt, Abstr., 1907, i, 310).—The formulæ for pyrene and pyrenic acid deduced by Goldschmiedt are confirmed by isolation of two isomeric methyl hydrogen pyrenates,

$$C_{16}H_{10}O_5.$$

The *α-ester*, prepared by heating the anhydride with a large excess of pure methyl alcohol, crystallises in large needles of a golden-yellow colour and yields golden-yellow solutions. The *β-ester* crystallises in yellowish-green, slender needles, usually arranged in nodules; its solutions are brownish-green, and it is twice as soluble in alcohol as the α-ester. When heated, the β-ester turns brown more rapidly than the α-ester, and decomposes more quickly.

peri-*Trimethylenenaphthalic anhydride* (formula I) is obtained when pyrenic acid is reduced by boiling with hydriodic acid (D 1·96)

and red phosphorus. It crystallises from alcohol in colourless, glistening needles, decomposing at about 260° Its solution in concentrated sulphuric acid has a deep blue fluorescence, and its alcoholic solution a green fluorescence. The corresponding *acid*, $C_{15}H_{12}O_4$, is colourless, and does not readily yield crystalline salts. When the barium salt is heated with lime, peri-*trimethylenenaphthalene*, $C_{13}H_{12}$, is obtained, and this crystallises from dilute alcohol in colourless, glistening plates, m. 68—69°. It turns yellow on exposure to the air, and yields a *picrate* in the form of glistening, red needles, m. p. 127° after turning brown at 80°. The formation of this picrate is used as an argument in favour of the constitutional formula ascribed to the hydrocarbon, as hydronaphthalenes do not yield picrates.


(I.)

Hexahydropyrene (Goldschmiedt, *loc. cit.*) has m. p. 129—130°, and in the presence of excess of picric acid yields a red *picrate*, m. p. 119°. The constitution ascribed to the hexahydro-compound is therefore that of a di*peri*ditrimethylenenaphthalene. J. J. S.

Reduction of Nitrobenzene to Aniline. C. Nicolescu Otin (*Zeitsch. Elektrochem.*, 1910, 16, 674—680).—The author has tried most of the methods which have been proposed for reducing nitrobenzene to aniline by electrolysis. His results are tabulated, and show that the yields of aniline are usually poor (from 19 to 88%); considerable quantities of other materials are consumed in many of the processes, and undesirable by-products are often formed. He shows that the conditions necessary for a good yield are a very large cathode surface and a considerable excess of hydrochloric acid.

Using 120 c.c. of hydrochloric acid (D 1·19) to 20 grams of nitrobenzene and a cathode consisting of lead wool, or nickel wire in sufficient quantity to fill the whole cathode compartment (the anode is a lead cylinder immersed in sulphuric acid contained in a porous pot), he obtains 92 to 94% of the theoretical quantity of aniline with a current efficiency of 94 to 97%. T. E.

[Chromoisomeric and Homochromoisomeric Nitroanilines.] Arthur Hantzsch (*Ber.*, 1910, 43, 2516. Compare this vol., i, 475). —The following corrections are made. Priority is given to Flürscheim in the preparation of *s*-nitrophenylenediamine. *o*-Tolyl-2 : 4-dinitroaniline darkens at 120°, and has m. p. 128—129°. Also, a reply is given to Busch (this vol., i, 617) on the isomerism of tho two picrylmethylanilines. C. S.

[Preparation of Derivatives of *p*-Toluenesulphon-*p*-nitroanilide.] Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 224499).—*p*-Toluenesulphon-*p*-nitroanilide when treated with methyl chloride yielded p-*toluenesulphonmethyl*-p-*nitroanilide*, m. p. 175—176°; this on reduction with sodium sulphide was converted into p-*toluenesulphonylmethyl*-p-*phenylenediamine*, m. p. 135°, a grey powder some-

what readily soluble in alcohol, more sparingly so in benzene. This base was diazotised and combined in alkaline solution with 8-acetylamino-1-naphthol-3 : 6-disulphonic acid (or similar acids), and the separated product treated during several hours with sulphuric acid at a temperature of 15—20°, whereby the toluenesulphonyl group only was eliminated; the final products were violet-blue dyes, very stable to alkalis and light. F. M. G. M.

Hyposulphites. VII. Rongalite and Salts of Amines. Arthur Binz and Th. Marx (*Ber.*, 1910, 43, 2344—2349. Compare Binz and Isaac, Abstr., 1908, i, 940).—The hydrochlorides of amines react with rongalite even in the absence of formaldehyde. It is suggested that the hydrochloride first condenses with the sodium salt according to the equation

$RNH_2,HCl + OH\cdot CH_2\cdot O\cdot S\cdot ONa = RNH\cdot CH_2\cdot O\cdot S\cdot OH + NaCl + H_2O$,

and that the substituted formaldehydesulphoxylic acid then forms a salt with the excess of the amine hydrochloride:

$RNH\cdot CH_2\cdot O\cdot S\cdot OH + RNH_2,HCl = RNH\cdot CH_2\cdot O\cdot S\cdot O\cdot NH_3R + HCl$,

and that it is this salt which is precipitated. In the case of ammonium chloride and of hydroxylamine hydrochloride, it has been found possible to isolate the intermediate product. The salts are decomposed by cold dilute sodium hydroxide solution, and practically half the amine used up in the formation of the compound is liberated.

Rongalite and *o*-toluidine hydrochloride yield the salt

$C_6H_4Me\cdot NH\cdot CH_2\cdot O\cdot SO\cdot NH_3\cdot C_6H_4Me$

in the form of colourless crystals, m. p. 101—104°. It turns a yellow colour on exposure to the air, and reduces warm indigocarmin solution. When an excess of rongalite is used, mixtures are formed.

Rongalite and anthranilic acid hydrochloride yield colourless crystals of the compound $C_{15}H_{16}O_6N_2S$, m. p. 143° (decomp.). When diazotised, it yields salicylic acid, and when oxidised with hydrogen peroxide or with sodium thiosulphate yields anthranilic acid. Rongalite and hydroxylamine hydrochloride in the presence of formaldehyde solution yield *hydroxylaminomethylsulphurous acid*, $OH\cdot NH\cdot CH_2\cdot O\cdot SO_2H$, owing to the oxidising action of the hydroxylamine. It can be crystallised from water, does not reduce indigocarmin, and has m. p. 191°. J. J. S.

Preparation of Thiodiphenylamine and its Derivatives. Fritz Ackermann (D.R.-P. 224348).—The preparation of thiodiphenylamines with the aid of sulphur and aluminium chloride has previously been described; it is now found that aluminium bromide or iodide, ferric chloride, antimony trichloride, cuprous iodide, sulphur iodide, or iodine can be employed equally well, and the methods of doing so with their extension to the preparation of thio-β-dinaphthylamine and thiophenyl-β-naphthylamine are described. *Thio*-p-*tolyl*-β-*naphthylamine* was obtained as a greenish-yellow powder, m. p. 182°. F. M. G. M.

Action of Magnesium Alkyl Halides on Anilides and their Chlorides. Max Busch and Martin Fleischmann (*Ber.*, 1910, 43, 2553—2556).—Béis has shown that the interaction of acid amides

and magnesium alkyl halides leads to the formation of ketones and ammonia (Abstr., 1904, i, 15). When the aminic hydrogen atoms are replaced by alkyl groups, the authors find that a dual reaction occurs; thus, magnesium phenyl bromide (2 mols.) and benzoylethylaniline in ether yield ultimately benzophenone and ethylaniline (from $OMgBr\cdot CPh_2\cdot NEtPh$), and also *triphenylmethylethylaniline*,

$$CPh_3\cdot NEtPh,$$

m. p. 92° (from $OMgBr\cdot CPh_2\cdot NEtPh$ and PhMgBr), which easily decomposes in alcoholic solution into triphenylcarbinol and ethylaniline.

Magnesium alkyl halides react with imino-chlorides generally either at the double linking or at the reactive halogen atom, yielding the same product in both cases, but sometimes at both of these points of attack. Thus benzanilideimino-chloride and ethereal magnesium methyl iodide yield ultimately acetophenoneanil, $NPh{:}CPhMe$, which cannot be isolated, but the presence of which is proved by hydrolysis with hydrochloric acid, whereby acetophenone and aniline are obtained. In a similar way the imino-chloride reacts with magnesium ethyl bromide to form ultimately an anil which yields aniline and phenyl ethyl ketone by hydrolysis, and with magnesium phenyl bromide to form ultimately benzophenoneanil, m. p. 113—114°; once in the latter preparation a considerable amount of triphenylmethylaniline, $CPh_3\cdot NHPh$, was obtained, but the conditions of its formation could not be repeated. C. S.

Metathetical Reactions: Ether-thiocarbamides and their Relation to ψ-Ammonium Bases. Treat B. Johnson and Herbert H. Guest (*J. Amer. Chem. Soc.*, 1910, 32, 1279—1285).—Cyclic quaternary bases (pyridines, quinolines, *iso*quinolines, and acridines) undergo isomeric change in aqueous solution, the hydroxyl group of the base migrating from the nitrogen to a carbon atom with formation of ψ-ammonium bases. The latter compounds react with alcohols at the ordinary temperature with loss of a molecule of water and production of alcoholates or ethers. When these alcoholates are warmed with alcohols, the alkyl group of the alcoholate is replaced by that of the alcohol. The mechanism of this change has been interpreted in different ways (compare Decker, Abstr., 1900, i, 522, and Gadamer, Abstr., 1905, i, 368; 1908, i, 322). In order to throw further light on these transformations, a study has been made of some ether-thiocarbamides.

The ether-thiocarbamides, $OR\cdot CH_2\cdot NH\cdot CS\cdot NHR'$, were obtained by the action of certain thiocarbimidomethyl ethers, $RO\cdot CH_2\cdot NCS$, on organic bases (Johnson and Guest, Abstr., 1909, i, 371). These substances are closely related to the cyclic alcoholates, as they contain the same complex, $\begin{matrix}|\\ {:}C\cdot N\cdot CH\cdot OR\\ |\quad |\end{matrix}$, and hence may be regarded as acyclic ψ-ammonium compounds. The ether-thiocarbamides would therefore be expected to undergo transformations with alcohols analogous to those which take place with the cyclic alcoholates, and such has been found to be the case. All the ether-thiocarbamides which have been examined react with alcohols on warming, with transposition of the alkyl groups. These reactions are reversible, and are not affected by

the b. p.'s of the alcohols or by the size of the alkyl groups involved. It is therefore possible to obtain a whole series of ether-thiocarbamides from one thiocarbimidomethyl ether. These transformations are most easily explained by assuming that unstable additive compounds are first formed, and that these decomposes with production of a new thiocarbamide and alcohol.

s-*Phenylmethoxymethylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot OMe$, m. p. 133°, obtained by recrystallising *s*-phenylethoxymethylthiocarbamide or *s*-phenyl*iso*amyloxymethylthiocarbamide from methyl alcohol, forms prismatic crystals. s-p-*Tolylmethoxymethylthiocarbamide*,

$$C_6H_4Me\cdot NH\cdot CS\cdot NH\cdot CH_2\cdot OMe,$$

m. p. 129°, is obtained by the action of methyl alcohol on the corresponding ethoxy-compound. E. G.

Replacement of Halogen by the Nitro-group. II. L. Chas. Raiford and Frederick W. Heyl (*Amer. Chem. J.*, 1910, **44**, 209—219).—It has been found previously (this vol., i, 373) that when 2 : 4 : 6-tribromophenol is treated with nitrous acid, a mixture of 4 : 6-dibromo-2-nitrophenol and 2 : 6-dibromo-4-nitrophenol is produced, but that 2 : 4 : 6-trichlorophenol is not affected by nitrous acid. In view of these results, it was considered of interest to study the behaviour of 2 : 4 : 6-tri-iodophenol. The work has also been extended to 2 : 4 : 6-tribromoresorcinol.

2 : 4 : 6-Tri-iodophenol has m. p. 158°, instead of 156°, as stated by Messinger and Vortmann (Abstr., 1889, 1150). The *acetate*, m. p. 154°, forms colourless needles. When sodium nitrite is added gradually to a solution of 2 : 4 : 6-tri-iodophenol in a mixture of glacial acetic acid and benzene at 12—15°, 4 : 6-di-iodo-2-nitrophenol is obtained, together with 2 : 6-*di-iodo*-4-*nitrophenol*, m. p. 155°, which forms nearly colourless prisms. It is probable that a small quantity of an iododinitrophenol is also produced in this reaction. On reducing 4 : 6-di-iodo-2-nitrophenol with stannous chloride in presence of hydrochloric acid, the *hydrochloride* of 4 : 6-di-iodo-2-aminophenol is obtained, which crystallises in long prisms.

When a solution of 2 : 4 : 6-tribromoresorcinol in glacial acetic acid is treated with sodium nitrite at 12—15°, 2 : 6-*dibromo*-4-*nitroresorcinol*, m. p. 148°, is produced, which forms maroon prisms or orange needles; its *ammonium* salt crystallises in deep yellow prisms. On reducing this nitro-compound with a solution of stannous chloride in hydrochloric acid, the *hydrochloride* of 2 : 6-*dibromo*-4-*aminoresorcinol* is obtained. 2 : 6-*Dibromo*-4-*aminoresorcinol* darkens above 135°, and decomposes above 175° without melting; it crystallises in prisms which are at first colourless, but soon become grey; the *picrate* begins to decompose at 220° without melting. 2 : 6-*Dibromo*-4-*acetylaminoresorcinyl diacetate*, m. p. 174—175°, forms colourless, hexagonal plates. E. G.

Preparation of *o*- and *p*-Nitrophenols. R. S. Hart (*J. Amer. Chem. Soc.*, 1910, **32**, 1105—1106).—Phenol (50 grams) dissolved in alcohol (5 grams) is added drop by drop (30 drops a minute) to a solution of sodium nitrate (80 grams) in sulphuric acid (100 grams) diluted with 200 c.c. of water at 25°. The mixture is stirred vigorously

during the addition, and for half an hour afterwards. After an hour and a-half, the liquid is treated in the usual way, and gives a yield of 30 grams of *o*-nitrophenol and 13 grams of *p*-nitrophenol. W. O. W.

Phenyl Ether and Some of its Derivatives. Alfred N. Cook (*J. Amer. Chem. Soc.*, 1910, **32**, 1285—1294).—The ethers used in this investigation were prepared by distilling the aluminium derivatives of the corresponding phenols. Good yields were obtained of phenyl and *m*-tolyl ethers, but only small yields of *o*- and *p*-tolyl ethers. On rapidly distilling aluminium *p*-tolyloxide, flashes appeared on the surface of the liquid. When some aluminium *p*-tolyloxide which had been exposed to the air for about two months was distilled, *p*-cresol was obtained, but very little *p*-tolyl ether. The causes of these phenomena are being investigated.

Tetrabromophenyl ether, $O(C_6H_3Br_2)_2$, b. p. 280—290°/25 mm., 410—425°/760 mm., m. p. 83—84°, prepared by slowly adding an excess of bromine to a solution of phenyl ether in carbon disulphide containing a little iodine to serve as a carrier, forms large needles. It was not found possible to obtain a more highly brominated derivative.

Dibromo-m-*tolyl ether*, $O(C_6H_3MeBr)_2$, b. p. about 250°/15 mm. and 340—350° (uncorr.)/760 mm., m. p. 48°, prepared by slowly adding the calculated quantity of bromine to a solution of *m*-tolyl ether in carbon disulphide, forms white crystals. *Tetrabromo*-m-*tolyl ether*, $O(C_6H_2MeBr_2)_2$, b. p. 260—270°/35 mm., is obtained by the action of an excess of bromine on *m*-tolyl ether in presence of a little iodine as a viscous substance which slowly crystallises. A more highly brominated derivative could not be obtained.

2 : 4-*Dinitrophenyl* p-*tolyl ether*, $C_6H_4Me\cdot O\cdot C_6H_3(NO_2)_2$, m. p. 93°, prepared by the action of potassium *p*-tolyloxide on 1-bromo-2 : 4-dinitrobenzene, forms yellow crystals. The *sulphonic acid*,

$$SO_3H\cdot C_6H_3Me\cdot O\cdot C_6H_3(NO_2)_2,$$

m. p. 150° (decomp.), crystallises in slender needles containing $1\frac{1}{2}H_2O$; its *barium* and *sodium* salts are described. When a solution of 2 : 4-dinitrophenyl *p*-tolyl ether in glacial acetic acid is warmed with chromic anhydride, it is converted into p-2 : 4-*dinitrophenoxybenzoic acid*, $CO_2H\cdot C_6H_4\cdot O\cdot C_6H_3(NO_2)_2$, a yellow substance which does not melt below 200°; its *silver* salt is described.

2 : 4-*Dinitrophenyl ether*, $C_6H_5\cdot O\cdot C_6H_3(NO_2)_2$, m. p. 70°, b. p. 230—250°/27 mm., obtained by the action of potassium phenoxide on 1-bromo-2 : 4-dinitrobenzene, is a crystalline substance with a faint odour and a pungent taste. The *sulphonic acid*, $SO_3H\cdot C_6H_4\cdot O\cdot C_6H_3(NO_2)_2$, forms white, pearly flakes; its *barium* salt is described. *Trinitrophenyl ether*, $C_{12}H_7O(NO_2)_3$, prepared by dissolving 2 : 4-dinitrophenyl ether in concentrated nitric acid, crystallises in clusters of yellow prisms.

A bibliography of phenyl ether and its derivatives is appended.

E. G.

Organic Compounds of Quadrivalent Tellurium. Charles Lederer (*Compt. rend.*, 1910, **151**, 611—612).—Tellurium tetrachloride (1 mol.) reacts with magnesium phenyl bromide (5 mols.) in

dry ether. In addition to chlorobenzene, diphenyl, and diphenyl telluride, the product yields a sparingly soluble material when treated with a limited amount of water. On treatment with aqueous potassium iodide this furnishes *diphenyltellurium di-iodide*, decomposing at 236—237°, and *triphenyltelluronium iodide*, $TePh_3I$. The latter crystallises in colourless needles, m. p. 247—248°, and on treatment with silver chloride or bromide gives the corresponding *chloride*, m. p. 244—245° (decomp.), and *bromide*, m. p. 259—260°.

Fixation of hydrogen chloride by diphenyltellurium leads to the formation of the *compound*, $TeHPh_2Cl$, m. p. 233—234°. W. O. W.

Preparation of Neutral Phenolic Esters of Diglycollic Acid. C. F. Boehringer & Söhne (D.R.-P. 223305).—The phenyl esters of diglycollic acid are readily prepared by treating the acid dichloride with the required phenol or sodium phenoxide (substituted or otherwise) in the presence of an indifferent base, such as dimethylaniline.

Diphenyl diglycollate, $O(CH_2{\cdot}CO_2Ph)_2$, forms colourless needles, m. p. 80°.

Disalicyl diglycollate forms colourless crystals, m. p. 173°; the *α-naphthyl* ester, colourless leaflets, m. p. 136°; the *β-naphthyl* ester, a colourless, crystalline powder, m. p. 160°; the *guaiacol* ester, colourless needles, m. p. 82°; the o-*tolyl* ester, needles, m. p. 101°; the m-*tolyl* ester, needles, m. p. 63°; the p-*tolyl* ester, needles, m. p. 89°; the o-*chlorophenyl* ester, needles, m. p. 129°; the p-*chlorophenyl* ester, slender needles, m. p. 130°; the o-*nitrophenyl* ester, colourless leaflets, m. p. 164°, and the p-*nitrophenyl* ester, a colourless, crystalline powder, m. p. 131°.

The solubility of these compounds in numerous solvents is fully described in the patent. F. M. G. M.

[Simple Formation of Benzyl Ethers.] Julius von Braun (*Ber.*, 1910, **43**, 2594).—Reply to Halban (this vol., i, 619). C. S.

The Addition of Bromine to Unsaturated Compounds. I. Allyl and Propenyl Derivatives of Benzene. Gino Abati (*Gazzetta*, 1910, **40**, ii, 89—94. Compare Abstr., 1909, i, 104).—A comparison of the velocity of addition of bromine in chloroform solution to chavicol and anethole, eugenol and *iso*eugenol and their methyl derivatives, safrole and *iso*safrole, myristicin and *iso*myristicin, and apiole and *iso*apiole, show that the velocity is always greater in the case of the propenyl derivative.

The molecular refractive indices of myristicin and *iso*myristicin have also been measured, and are found to be M_α 89·44 and M_α 92·94 respectively. C. H. D.

The Xylenol from Dehydracetic Acid. Emilio Carlinfanti and A. Germain (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 234—239).—The xylenol produced when dehydracetic acid is distilled with calcium oxide is not *o*-4-xylenol, as stated by Tivoli (Abstr., 1891, 1455), but the 1 : 3 : 5-compound. The mistake is due to the fact that a substance is also formed which gives a reaction

with ferric chloride similar to that of *o*-4-xylenol, and this impurity can only be removed by repeated crystallisation. When calcium acetate is heated with calcium oxide, a yellow *oil*, b. p. 215—225°, is obtained, which has no phenolic properties, but gives an intense coloration with ferric chloride. To explain the formation of *m*-5-xylenol, the following mechanism is suggested. Dehydracetic acid under the conditions of the experiment yields acetyltriacetic acid, which loses carbon dioxide and is converted into diacetylacetone, which decomposes into acetic acid and acetylacetone; this then condenses with the acetone formed from the calcium acetate. In confirmation of this view, the authors find that *m*-5-xylenol is produced when a mixture of the vapours of these two substances is led over calcium oxide at 400°.

5-*Hydroxy*-m-*xylyl phenylcarbamate*. $C_8H_9O\cdot CO\cdot NHPh$, crystallises in shining needles, m. p. 148—149°. R. V. S.

Fluorenyl Ethers. Alfred Kliegel (*Ber.*, 1910, 43, 2488—2496. Compare Abstr., 1905, i, 187).—Schmidt and Stützel (this vol., i, 29) on reducing fluorenoneoxime by tin and hot concentrated hydrochloric acid obtained fluorenyl ether, possessing a red colour, and quite different from the fluorenyl ether obtained by Barbier from fluorenyl alcohol. This red compound, the colour of which was attributed to the accumulation of benzene nuclei, is not in agreement with Witt's theory of colour.

By the action of silver oxide on 9-chlorofluorene, fluorenyl ether was obtained in colourless, lustrous plates, m. p. 228°, and it is further shown that the red compound of Schmidt and Stützel is in reality diphenylene-phenanthrone, m.p. 257°, coloured red by admixture with di-biphenylene ethylene, m. p. 187°.

The first product of the action of hydrochloric acid and tin, or, better, of stannous chloride, is a glistening, red, crystalline compound, which is a *stannichloride* of 9-*iminofluorene*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C\cdot NH$. The *picrate* crystallises in lustrous, orange needles, and when decomposed with ammonia yields the crystalline base, which separates in pale straw-yellow, slender needles, m. p. 124°. On warming with water, it readily decomposes into ammonia and ketone. An egg-yellow and an orange *oxalate* and a similarly coloured *sulphate* were also isolated. The *acetate* crystallises in citron-yellow needles, m. p. 104°. E. F. A.

[*m*-**Hydroxyphenyl Mercaptan.**] Ladislaus von Szathmáry (*Ber.*, 1910, 43, 2485—2487).—Sodium *m*-benzenedisulphonate was converted into sodium *m*-phenolsulphonate, and this into the *sulphonyl chloride*, which was obtained as a viscid, oily, brown product having a pungent, disagreeable odour. It is reduced by tin and hydrochloric acid to m-*hydroxyphenyl mercaptan*. This crystallises when strongly cooled, but is oily at the ordinary temperature. It has a pungent, unpleasant odour, and with lead acetate yields an insoluble, stable, yellow precipitate of the *lead* salt, $Pb(S\cdot C_6H_4\cdot OH)_2$. It shows no coloration with either sulphuric acid or sodium hydroxide. E. F. A.

Symmetrical Trithiophenols. Jacques Pollak and R. Tucaković (*Monatsh.*, 1910, **31**, 695—707).—*Trithiomethylphloroglucinol* [*toluene-2 : 4 : 6-trithiol*], $C_6H_2Me(SH)_3$, prepared by reducing *o*-tolyl-2 : 4 : 6-trisulphonyl chloride with tin and hydrochloric acid, forms white needles, m. p. 49—53°, having a characteristic odour. It readily undergoes oxidation, either on exposure to the air or under the action of oxidising agents, with the formation of yellow to yellowish-red products. With lead acetate, it gives a yellow precipitate, which quickly changes to red. In glacial acetic acid solution, it is readily transformed into the original trisulphonyl chloride by the action of chlorine.

The *triacetyl* derivative, $C_6H_2Me(SAc)_3$, forms needles, m. p. 93—95°, and is readily obtained by heating with acetic anhydride and fused sodium acetate. The *trimethyl ether*, $C_{10}H_{14}S_3$, prepared by the action of diazomethane in ethereal solution, or of methyl iodide in alkaline alcoholic solution, forms slender needles, m. p. 61—63°; it cannot be obtained by the action of hydrogen chloride and methyl alcohol. Trithiomethylphloroglucinol consequently behaves as a non-tautomeric phenol.

The condensation product with chloroacetic acid,

$$C_6H_2Me(S\cdot CH_2\cdot CO_2H)_3,$$

has m. p. 197—200°; the *ethyl* ester, $C_6H_2Me(S\cdot CH_2\cdot CO_2Et)_3$, has m. p. 30—35°.

The action of cold concentrated nitric acid (D 1·4) on the trimethyl ether gives rise to the *mononitro*-derivative, $NO_2\cdot C_6HMe(SMe)_3$, yellow prisms, m. p. 84—87°. With hot concentrated nitric acid or cold fuming nitric acid, a *monosulphoxide* of the above-mentioned nitro-derivative is produced, $NO_2\cdot C_6HMe\cdot(SMe)_2\cdot SOMe$, which forms slender, yellow needles, m. p. 178·5—179·5°. The position of the sulphoxide group has not been ascertained. Hot fuming nitric acid also gives rise to a substance, m. p. 235—237°, which requires further investigation.

Trithiophloroglucinol (Abstr., 1909, i, 761) has now been obtained in the form of white needles, m. p. 57—60°. The product,

$$C_6H_3(S\cdot CH_2\cdot CO_2H)_3,$$

obtained with chloroacetic acid forms white, silky needles, m. p. 179—180°, from which the *ethyl* ester was obtained as an oil. The trimethyl ether gives the *mononitro*-derivative, $NO_2\cdot C_6H_2(SMe)_3$, with cold concentrated nitric acid; it forms dark yellow, slender needles, m. p. 148—150°. T. S. P.

Cholesterol. II. Leo Tschugaeff and W. Fomin (*Annalen*, 1910, **375**, 288—297. Compare this vol., i, 31, 479).—In addition to work already recorded, the paper contains the following results. *Ethyl cholesterylxanthate*, $C_{27}H_{45}O\cdot CS\cdot SEt$, m. p. 141·5°, and the *propyl* ester, m. p. 135°, have almost the same dispersion coefficient as the methyl ester. *Cholesterylxanthamide*, $C_{27}H_{45}O\cdot CS\cdot NH_2$, m. p. 227°, is obtained by digesting the methyl ester with about 10% alcoholic ammonia for many days.

The constitutions of α-cholesterylene, cholesterol, β-cholesterylene,

and cholestane are represented respectively by: $R<^{-CH}_{CH_2}>CH$, $R<^{CH_2}_{CH_2}>CH\cdot OH$, $R<^{CH_2}_{-CH}>CH$, and $R<^{CH_2}_{CH_2}>CH_2$, where R is $CH_2Pr^{\beta}\cdot CH_2$
$CH_2{:}CH>C_{17}H_{26}$.

C. S.

Aromatic Fluorine Derivatives and Estimation of Fluorine in the Same. Hans Meyer and Alfred Hub (*Monatsh.*, 1910, 31, 933—938).—The three fluorobenzoic acids can be prepared readily by the oxidation of the fluorotoluenes with permanganate (compare Hollemann, Abstr., 1905, i, 425). The *o*-acid has m. p. 122°. The corresponding fluorobenzoyl chlorides, $C_6H_4F\cdot COCl$, can be obtained by the action of thionyl chloride on the acids. They are colourless, strongly refractive liquids with an odour resembling that of benzoyl chloride. The *o*-compound has b. p. 204° and m. p. 4°; the *m*-compound, b. p. 189° and m. p. – 30°, and the *p*-compound, b. p. 191—192° and m. p. 9°.

The *methyl* esters, $C_6H_4F\cdot CO_2Me$, have boiling points and melting points as follows: ortho, 207°, – 20°; meta, 194—195°, – 10°, and para, 197°, 4·5°. Some of these compounds have lower b. p.'s than the unsubstituted derivatives.

o-Fluorobenzamide, $C_6H_4F\cdot CO\cdot NH_2$, crystallises from water in colourless needles, m. p. 114°; the *meta*-compound in colourless plates, m. p. 128—129°, and the *para*-compound in colourless needles, m. p. 153°.

In estimating the fluorine in these compounds, the substance is heated with lime in a nickel tube, 40 cm. long and 4—5 mm. diameter, the end of which is closed by means of silver solder. The tube is treated in much the same manner as in the estimation of halogens by the lime method; it is necessary, however, to see that the lime is completely soluble in dilute acetic acid, and a temperature of 1000° must be attained in all parts of the tube. At the end the calcium fluoride is estimated in the usual manner. J. J. S.

Condensation Products of Anthranilic Acid with Aromatic Aldehydes. Hugo Wolf (*Monatsh.*, 1910, 31, 903—916).—Various aromatic aldehydes have been condensed with anthranilic acid in alcoholic solution in order to determine whether the resulting Schiff's bases exist in stereoisomeric forms (compare Hantzsch and Schwab, Abstr., 1901, i, 378; Anselmino, *ibid.*, 1907, i, 913; Manchot and Furlong, *ibid.*, 1909, i, 805; this vol., i, 33).

Two isomeric forms were observed in the anils obtained by the condensation of the acid with *o*- and *p*-hydroxybenzaldehydes.

Benzylideneanthranilic acid, $CHPh{:}N\cdot C_6H_4\cdot CO_2H$, crystallises in sulphur-yellow needles, m. p. 128°; *p-tolylideneanthranilic acid*, $C_6H_4Me\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, forms lemon-yellow, rectangular plates, m. p. 154°; *o-nitrobenzylideneanthranilic acid*,

$$NO_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CO_2H,$$

crystallises in yellow needles, m. p. 172°, and readily turns red on

exposure to the air; the isomeric *para*-compound forms pale yellow plates, m. p. 162°, and the *meta*-derivative, pale yellow needles, m. p. 206°.

Salicylideneanthranilic acid, $OH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, separates as small, yellow plates, m. p. 193°, when its alcoholic solution is cooled rapidly, otherwise the red modification, which crystallises in stout prisms, m. p. 200°, is obtained. The yellow crystals are transformed into the red when dissolved in amyl alcohol and the solution cooled slowly, or when the solution is cooled quickly and the yellow crystals left in contact with the amyl alcohol mother liquor for several hours. *p-Hydroxybenzylideneanthranilic acid* exists in yellow and red modifications, of which the red is the less stable. The yellow form is more readily soluble in ether than the red, and has m. p. 224°. The isomeric *m-hydroxy*-derivative crystallises in yellow prisms, m. p. 182°.

o-Methoxybenzylideneanthranilic acid, $OMe\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, forms yellow needles, m. p. 128°; the isomeric *para*-compound crystallises in yellow, rectangular plates, m. p. 142°, which turn red on exposure to the air. *Dimethylaminobenzylideneanthranilic acid*,

$$NMe_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CO_2H,$$

forms brick-red prisms, m. p. 214°.

3 : 4-Dihydroxybenzylideneanthranilic acid,

$$C_6H_3(OH)_2\cdot CH{:}N\cdot C_6H_4\cdot CO_2H,$$

crystallises in glistening, red needles, m. p. 226° (decomp.). *4-Hydroxy-3-methoxybenzylideneanthranilic acid*,

$$OMe\cdot C_6H_3(OH)\cdot CH{:}N\cdot C_6H_4\cdot CO_2H,$$

forms slender, lemon-yellow needles, m. p. 164°. *3 : 4-Piperonylideneanthranilic acid*, $CH_2O_2{:}C_6H_3\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, forms pale yellow, rectangular plates, m. p. 188°. *Cinnamylideneanthranilic acid*, $CHPh{:}CH\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, crystallises from toluene or ethyl acetate in yellow prisms, m. p. 156°. When heated at 100°, it begins to turn red, and gives an odour of cinnamaldehyde.

When alcoholic solutions of these anil acids are heated with the equivalent amount of phenylhydrazine for about thirty minutes on the water-bath, the $:N\cdot C_6H_4\cdot CO_2H$ group is replaced by the

$$:N\cdot NHPh$$

group, and the phenylhydrazones of the aldehydes are obtained.

J. J. S.

Lactonoid Anhydrides of Acylated Amino-acids. V. Lactone of *r*-Benzoylphenylalanine. Ernst Mohr and Fr. Siroschein (*J. pr. Chem.*, 1910, [ii], **82**, 322—335. Compare this vol., i, 483, 557).—Much of the work has been recorded (Abstr., 1909, i, 581). The ethyl ester, chloride, and amide of benzoylphenylalanine (Max, Abstr., 1909, i, 926) are conveniently prepared from the lactone; also the *anilide*, $CH_2Ph\cdot CH(NHBz)\cdot CO\cdot NHPh$, m. p. 233—234°, from the lactone and aniline in dry ether. *Benzoylphenylalanylglycine*, $CH_2Ph\cdot CH(NHBz)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 240—242° (decomp., softening at 185°), is obtained from glycine and the lactone of benzoylphenylalanine at 130°, or, better, in aqueous acetone in the presence of sodium hydroxide.

C. S.

o-Aminobenzyl Cyanide [*o*-Aminophenylacetonitrile] and its Conversion into 2-Aminoindole and Indole. Robert Pschorr and Gerh. Hoppe (*Ber.*, 1910, 43, 2543—2552).—The conversion of *o*-aminocinnamonitrile into 2-aminoquinoline by acids or alkalis (Pschorr, Abstr., 1898, i, 491) induced the authors to examine the behaviour of *o*-aminophenylacetonitrile under similar conditions. This substance is conveniently prepared by converting *o*-nitrophenylacetic acid by a suspension of phosphorus pentachloride in ether into the chloride, a solution of which in benzene and ether is converted by ammonia into *o-nitrophenylacetamide*, m. p. 160°; the amide is converted by thionyl chloride into the nitrile, an alcoholic solution of which is reduced by stannous chloride and concentrated hydrochloric acid to *o-aminophenylacetonitrile*, m. p. 72°, which is best isolated by treating an aqueous solution of its stannichloride with 30% sodium hydroxide, whereby the substance separates in almost quantitative yield. The presence of the "activated" methylene group in the ortho-position to the amino-group renders derivatives of the substance very liable to intramolecular condensation. Thus a solution of *o*-aminophenylacetonitrile in *N*-hydrochloric acid is converted into *indazolecarboxylonitrile*, $C_6H_4<\begin{matrix}C(CN)\\ |\\ N\end{matrix}>NH$, m. p. 140°, whilst a solution in ether yields by treatment with sodium and amyl formate, *indole-3-carboxylonitrile*, m. p. 178°. This nitrile forms an *acetyl* derivative, m. p. 202°, which is also obtained when *indole-3-aldoxime*, m. p. 197—200°, is heated with acetic anhydride.

o-Aminophenylacetonitrile yields a *formyl* derivative,

$$CN\cdot CH_2\cdot C_6H_4\cdot NH\cdot CHO,$$

m. p. 110°, which shows no tendency to intramolecular condensation, and is simultaneously hydrolysed and converted into 2-aminoindole by boiling potassium carbonate; an *acetyl* derivative, m. p. 120°, and a *diacetyl* derivative, m. p. 80°.

By treatment with boiling alcoholic sodium ethoxide in an atmosphere of hydrogen, *o*-aminophenylacetonitrile is converted into *2-aminoindole*, $C_6H_4<\begin{matrix}CH\\ |\\ NH\end{matrix}>C\cdot NH_2$, which separates from water in prisms containing H_2O, has a strongly alkaline reaction, is reduced by sodium and alcohol to indole, and forms a *diacetyl* derivative, m. p. 142°, which is converted by aqueous potassium carbonate into *2-acetylaminoindole*, m. p. 167°. When an ethereal solution of 2-aminoindole is treated with ethyl chloroformate, three products are obtained, two of which, m. p. 93° and 160° respectively, are isomeric and contain two carbethoxy-groups, whilst the third has m. p. 145—150° and contains only one carbethoxy-group. The constitution of 2-aminoindole is proved by the fact that Piccini and Salmoni's indole-2-urethane, by treatment with ethyl chloroformate, yields the isomeride, m. p. 93°, containing two carbethoxy-groups, mentioned above. C. S.

Action of Thionyl Chloride on Benzilic Acid. Robert Stollé (*Ber.*, 1910, 43, 2471—2473).—By the interaction of thionyl chloride and benzilic acid in carbon tetrachloride solution at the ordinary temperature, α-chlorodiphenylacetic acid is formed. When the con-

stituents are boiled some days in the same solvent, *α-chlorodiphenylacetic anhydride*, $(CPh_2Cl\cdot CO)_2O$, is formed, m. p. 129°. This compound also arises when α-chlorodiphenylacetic acid is warmed with thionyl chloride. With aniline in ethereal solution, α-anilinodiphenylacetic acid, m. p. 168°, and *α-anilinodiphenylacetic anhydride*, crystallising in minute needles, m. p. 181°, and insoluble in sodium hydroxide, are formed.

A by-product of the action of thionyl chloride on benzilic acid crystallises in compact crystals insoluble in sodium carbonate, m. p. 119°. This is possibly *tetraphenyldiglycollyl chloride*, $C_{28}H_{30}O_3Cl_2$; it forms an anilide, m. p. 134°.

On shaking chlorodiphenylacetic anhydride in ether with sodium carbonate, an amorphous compound, probably benzilic anhydride, m. p. about 90°, is obtained. When heated with yellow mercuric oxide, chlorodiphenylacetic anhydride yields benzilide, m. p. 194°, which probably has the constitution of tetraphenyldiglycollic anhydride.

E. F. A.

Action of Dichloroacetic Acid on Aniline and its Homologues. III. Gustav Heller with Salo Aschkenasi (*Annalen*, 1910, 375, 261—288. Compare Abstr., 1908, i, 216).—The paper contains a repetition of some of the earlier work in order to controvert Ostromisslensky's views of the course of the reaction between dichloroacetic acid and aniline or its homologues (Abstr., 1908, i, 82, 888, 889).

The reaction between dichloroacetic acid and *p*-anisidine furnishes the only case in which the initial product of the reaction has been isolated; *di*-p-*anisidinoacetic acid*, $CO_2H\cdot CH(NH\cdot C_6H_4\cdot OMe)_2$, m. p. 201—202°, forms a *hydrochloride*, $C_{16}H_{18}O_4N_2,HCl$, m. p. about 215°, cannot be diazotised or benzoylated, and does not form a nitrosoamine. The product of the reaction between dichloroacetic acid and *o*-toluidine is not *o*-methylaminophenyl-*o*-toluidinoacetic acid (Ostromisslensky, *loc. cit.*), but 2 : 2′-*diaminoditolyl*-4 : 4′-*acetic acid*,

$$CO_2H\cdot CH(C_6H_3Me\cdot NH_2)_2,$$

since it requires 2 mols. of sodium nitrite for diazotisation, and the diazotised product yields *bis-β-naphtholazodi-o-tolylacetic acid*,

$$C_{30}H_{28}O_4N_4,$$

m. p. 195°, *bis*-6-*sulpho-β-naphtholazodi-o-tolylacetic acid*,

$$C_{36}H_{28}O_{10}N_4S_2,$$

and *bis*-3 : 6-*disulpho-β-naphtholazodi-o-tolylacetic acid*,

$$C_{30}H_{28}O_{16}N_4S_4,$$

with β-naphthol, β-naphthol-6-sulphonic acid, and β-naphthol-3 : 6-disulphonic acid respectively. 2 : 2′-Diaminoditolyl-4 : 4′-acetic acid yields only a *monobenzoyl* derivative, m. p. 242—243°, by the Schotten-Baumann method; when benzoylated in the presence of sodium hydrogen carbonate, it yields a mixture of the preceding compound and an anhydro-derivative, $C_{23}H_{20}O_2N_2$, thereof.

2 : 2′- *Diamino-di*-m-*xylyl*-4 : 4′-*acetic acid*,

$$CO_2H\cdot CH(C_6H_2Me_2\cdot NH_2)_2,$$

m. p. 241°, obtained from aqueous potassium dichloroacetate, sodium acetate, and *m*-2-xylidine on the water-bath, or from an acetic acid solution of the base and glyoxylic acid at the ordinary temperature,

forms a *dibenzoyl* derivative, $C_{32}H_{30}O_4N_2$, m. p. 272° (decomp.), with benzoyl chloride in aqueous potassium hydroxide, an *anhydrobenzoyl* derivative, $C_{25}H_{24}O_2N_2$, unchanged at 300°, with benzoyl chloride in cold pyridine, and combines, after being diazotised, with β-naphthol-6-sulphonic acid in sodium carbonate solution to form a normal *bisazo*-compound, $C_{33}H_{32}O_{10}N_4S_2$, the combination in a solution of an alkali hydroxide yielding a black substance.

The usual reaction between dichloroacetic acid and ψ-cumidine yields 3-*ψ-cumidino*-4 : 5 : 7-*trimethyloxindole*,

$$C_6HMe_3\begin{<}CH(NH\cdot C_6H_2Me_3)\\NH\end{>}CO,$$

decomp. 205°; this is oxidised by iodine in glacial acetic acid to 4 : 5 : 7-*trimethylisatin*, $C_6HMe_3\begin{<}CO\\NH\end{>}CO$, m. p. 276°, which forms red needles, yields a *phenylhydrazone*, m. p. 248°, and is so stable to alkalis that the pyrrole nucleus is only ruptured at 50°.

The product of the direct action of dichloroacetic acid on aniline is not 4 : 4′-diaminodiphenylacetic acid (Ostromisslensky, *loc. cit.*), but its hydrochloride (Heller, Abstr., 1909, i, 20); the free acid has m. p. 195°, forms a *diacetyl* compound, m. p. 231°, and yields a *dibenzoyl* derivative, decomp. 256°, with benzoyl chloride and sodium hydroxide, and an *anhydrobenzoyl* derivative, $C_{21}H_{16}O_2N_2$, softening at 225°, with benzoyl chloride in cold pyridine. The product obtained by the addition of a dilute acetic acid solution of aniline to aqueous glyoxylic acid is aniline anilglyoxylate, not dianilinoacetic acid (Ostromisslensky, Abstr., 1908, i, 889), because only 1 mol. of aniline is eliminated by cold sodium carbonate. C. S.

Preparation of Oxyarylurethane Carbamido- and Thiocarbamido-cinnamic Acid Esters. Gesellschaft für Chemische Industrie in Basel (D.R.-P. 224107).—Cinnamic acid esters of the general formula $C_6H_5\cdot CH{:}CH\cdot CO\cdot O\cdot R\cdot NH\cdot C\begin{<}X\\Y\end{>}$ (where R is an aromatic radicle, X oxygen or sulphur, Y an alkyloxy-, amino-, or alkylamino-group) are readily prepared when cinnamoyl chloride is heated with *p*-hydroxyphenyl-carbamide or -urethanes; they are of great value in the treatment of tubercular complaints, and in surgery.

p-*Cinnamoyloxyphenylcarbamide*, colourless needles, m. p. 203°, is prepared by heating (or allowing to remain at the ordinary temperature) cinnamoyl chloride with *p*-hydroxyphenylcarbamide in aqueous alkaline solution.

m-*Cinnamoyloxyphenylcarbamide* has m. p. 204—205°.

p-*Cinnamoyloxyphenylurethane*, colourless needles, m. p. 150—151°, is prepared from the foregoing acid chloride and *p*-hydroxyphenylurethane, $OH\cdot C_6H_4\cdot NH\cdot CO_2Et$. o-*Cinnamoyloxyphenylurethane* has m. p. 101—102°.

p-*Cinnamoyloxyphenylallylcarbamide*,

$$CHPh{:}CH\cdot CO\cdot O\cdot C_6H_4\cdot NH\cdot CS\cdot NH\cdot C_3H_5,$$

m. p. 129—130°, is prepared in analogous manner from *p*-hydroxyphenylallylthiocarbamide in acetone solution.

Cinnamic anhydride, or the acid in the presence of phosphoryl

chloride, can also be employed for this condensation, likewise other hydroxyphenylcarbamido-derivatives. F. M. G. M.

Melting Point of Granules of Salol. P. N. Pawloff (*Zeitsch. physikal. Chem.*, 1910, 74, 562—566. Compare Abstr., 1908, ii, 927).—The relationship between the melting point of salol particles and their magnitude has been further investigated by heating commercial salol for long periods at constant temperatures, and determining by microscopic observation the surface area of the largest crystals which formed as a result of fusion and subsequent crystallisation. It was found necessary to heat for about two and a-half hours in order to obtain the maximum size of crystals.

The more fusible portion was investigated between 34·8° and 37·8° by the method described. The maximum crystal at 37·8° had a surface of 1296 sq. μ; the maximum formed at 34·8° a surface of 228 sq. μ. The less fusible portion was investigated between 39° and 41°. At the former temperature, particles of surface 200 sq. μ, at the latter temperature, particles of surface 1328 sq. μ, remain unaltered. The relative size of the crystals cannot readily be determined, but from the data obtained for the less fusible portion it is estimated that when the specific surface is increased one hundred times by dividing up the particles, the melting point is lowered by 2·8°. G. S.

Preparation of Monoiodosalicylic Acids or its Nuclear Homologues. Max Haase (D.R.-P. 224536. Compare Lassar-Cohn and Fritz Schultze, Abstr., 1905, i, 893).—The methods that have previously been employed for the preparation of monoiodosalicylic acids have given poor yields and impure products; the one now described is that whereby an alkaline solution of sodium salicylate is slowly treated with a very slight excess of iodine dissolved in potassium iodide at the ordinary temperature and with continual stirring; colourless needles, m. p. 197°, were obtained. Three iodosalicylic acids with m. p.'s 198°, 196°, and 199·5° have previously been described in the literature. F. M. G. M.

Preparation of Amides of Monoiodosalicylic Acid and its Homologues. Max Haase (D.R.-P. 224346).—The amides of iodosalicylic acid (or other hydroxycarboxylic acids) can be readily prepared by treating the respective acid amide with potassium iodide and iodine in alkaline solution and allowing the mixture to remain at the ordinary temperature.

Iodosalicylamide, colourless leaflets, m. p. 230—231°, is sparingly soluble in hot water, and of therapeutic value. F. M. G. M.

Preparation of 5-Iodo-2-acetoxybenzoic Acid. Max Haase (D.R.-P. 224537).—The attempted preparation of iodoacetoxybenzoic acid from acetoxybenzoic acid results in the elimination of the acetyl group; it is now found that acetylation of iodosalicylic acid yields the required product.

5-Iodo-2-acetoxybenzoic acid, colourless needles, m. p. 175°, is prepared by boiling iodosalicylic acid with acetic anhydride in the presence

of anhydrous sodium acetate during three hours; it is a very important therapeutic agent, comparing favourably with *o*-acetoxybenzoic acid (aspirin) in being tasteless and less readily hydrolysed.

F. M. G. M.

Preparation of Acylsalicylic [*o*-Acyloxybenzoic] Anhydrides. Alfred Einhorn (D.R.-P. 224844).—When the carbonyl esters of acylsalicylic acids (usually oils) having the general formula $OX\cdot C_6H_4\cdot CO\cdot O\cdot CO_2R$ (R = alkyl; X = acyl) are heated, they yield the corresponding crystalline acyl salicylic anhydride.

o-Acetoxybenzoic anhydride, glistening needles, m. p. 85°, is prepared by heating *o*-acetoxybenzoic acid with ethyl chlorocarbonate in benzene or ethereal solution in the presence of a tertiary base, such as pyridine; the *ethyl* o-*acetoxybenzoylcarbonate*, $OAc\cdot C_6H_4\cdot CO\cdot O\cdot CO\cdot OEt$, is isolated in the form of a viscid oil, which, when heated during ten to twenty-four hours on the water-bath, is transformed into the foregoing anhydride.

Benzoyloxybenzoic anhydride, prismatic needles, m. p. 109—111°, is similarly obtained from *ethyl* o-*benzoyloxybenzoylcarbonate*,

$$OBz\cdot C_6H_4\cdot CO\cdot O\cdot CO_2Et.$$

o-*Cinnamoyloxybenzoic acid anhydride*, slender needles, m. p. 110—112°, from *ethyl* o-*cinnamoyloxybenzoylcarbonate*, m. p. 53—55°. These compounds are of therapeutic value. F. M. G. M.

The *N*-Methyl Derivatives of Phenylalanine and Tyrosine. Ernst Friedmann and S. Gutmann (*Biochem. Zeitsch.*, 1910, **27**, 491—497).—In connexion with earlier experiments on the behaviour of methylated amino-acids in the animal body (Friedheim, Abstr., 1908, ii, 205), the authors have prepared the methyl derivatives of the aromatic amino-acids occurring in proteins. *α-Methylamino-β-phenylpropionic acid* (*phenyl*-N-*methylalanine*), $CH_2Ph\cdot CH(NHMe)\cdot CO_2H$, prepared from aqueous methylamine and α-bromo-β-phenylpropionic acid, crystallises in three-sided plates subliming at 252—254° (decomp.).

p-*Methoxybenzylmalonic acid*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)_2$, prepared by reducing anisylidenemalonic acid with sodium amalgam by Knoevenagel's condensation, crystallises in large, irregular plates, m. p. 118·5° (decomp.). On treatment with bromine, it yields the *α-bromo*-derivative, $OMe\cdot C_6H_4\cdot CH_2\cdot CBr(CO_2H)_2$, which crystallises in four-sided leaflets decomposing at 153°. On heating at 120—130° with a little water, this gives *α-bromo-β*-p-*methoxyphenylpropionic acid*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CHBr\cdot CO_2H,$$

a brown, viscid oil, which with methylamine furnishes *α-methylamino-β*-p-*methoxyphenylpropionic acid*, crystallising in colourless scales, m. p. 256—257° (decomp.). This, on hydrolysis with hydrobromic acid, gives *α-methylamino-β*-p-*hydroxyphenylpropionic acid* (N-*methyltyrosine*), $OH\cdot C_6H_4\cdot CH_2\cdot CH(NHMe)\cdot CO_2H$, which crystallises in bunches of blunt needles, m. p. 318°. G. S. W.

2-Naphthol-3-carboxylic Acid and its Condensation with Benzaldehyde. Franz Friedl (*Monatsh.*, 1910, **31**, 917—932. Compare J. Schmid, Abstr., 1893, i, 475; Möhlau, *ibid.*, 1896, i, 243).—The ketonic formula for 2-naphthol-3-carboxylic acid is some-

what analogous to that of benzyl methyl ketone; the condensation of benzaldehyde with methyl 2-naphthol-3-carboxylate in the presence of hydrogen chloride has been studied, and has been found to be of the same type as the condensation of benzyl methyl ketone and benzaldehyde in the presence of hydrogen chloride (Goldschmiedt and Krczmar, Abstr., 1901, i, 40), the resulting compound being methyl α-chloro-1-benzyl-2-naphthol-3-carboxylate, $C_6H_4<\begin{matrix}C(CHPhCl):C\cdot OH\\ CH=\!=\!=\!=C\cdot CO_2Me\end{matrix}$, or the tautomeric ketone. The halogen atom in this compound is extremely reactive, and can be replaced readily by hydroxyl, methoxy-, phenoxy-, amino-, and anilino-groups (compare Braun, this vol., i, 479).

Methyl 2-naphthol-3-carboxylate has m. p. 73°.

Methyl α-chloro-1-benzyl-2-naphthol-3-carboxylate, $C_{19}H_{15}O_3Cl$, formed when dry hydrogen chloride is passed into a solution of methyl 2-naphthol-3-carboxylate in benzaldehyde at 0°, and the saturated solution kept for twenty-four hours, crystallises from perfectly dry benzene in microscopic prisms, m. p. 160—161°. At higher temperatures it loses hydrogen chloride, and at 220—225° is completely decomposed.

The corresponding *bromo*-derivative, $C_{19}H_{15}O_3Br$, has m. p. 183°; the hydroxy-derivative, *methyl 1-α-hydroxybenzyl-2-naphthol-3-carboxylate*, $C_{19}H_{16}O_4$, crystallises from benzene in pale yellow, glistening prisms, m. p. 173—174°. *Methyl 1-α-acetoxybenzyl-2-naphthol-3-carboxylate*, obtained by the action of acetic anhydride on the hydroxy-compound, forms pale yellow prisms, m. p. 136—137°. *Methyl α:2-diacetoxy-1-benzyl-3-naphthoate* has m. p. 70—73°, and decomposes at 85°. *Methyl 1-α-methoxybenzyl-2-naphthol-3-carboxylate*, $C_{20}H_{18}O_4$, prepared by the action of methyl alcohol on the chloro-derivative, crystallises from a mixture of benzene and alcohol in yellow, flat prisms, m. p. 177°. The corresponding *ethoxybenzyl* derivative, $C_{21}H_{20}O_4$, has m. p. 116—117°, and the *phenoxybenzyl* compound, $C_{25}H_{20}O_4$, m. p. 188°.

Methyl 1-α-aminobenzyl-2-naphthol-3-carboxylate, $C_{19}H_{17}O_3N$, crystallises from a mixture of chloroform and alcohol in yellow, microscopic prisms, m. p. 220°; the corresponding *anilinobenzyl* derivative,

$$C_{25}H_{21}O_3N,$$

crystallises in small prisms, m. p. 214°, and yields a *hydrochloride*,

$$C_{25}H_{21}O_3N,HCl,$$

in the form of colourless crystals, m. p. 175° (decomp.).

1-Benzyl 2-naphthol-3-carboxylic acid, $C_{18}H_{14}O_3$, obtained by heating the methyl ester of the chloro-acid with hydriodic acid, crystallises in lemon-yellow needles, m. p. 224°, and gives a blue coloration with ferric chloride; the *acetyl* derivative, $C_{20}H_{16}O_4$, forms colourless, glistening needles, m. p. 166°, and the *methyl* ester, $C_{19}H_{16}O_3$, microscopic, yellow needles, m. p. 107°.

Most of the compounds are probably equilibrium mixtures of the ketonic and enolic forms. J. J. S.

Condensation of Diphenyleneglycollic Acid with Phenols and Phenol Ethers. Augustin Bistrzycki and Franz von Weber (*Ber.*, 1910, **43**, 2496—2505).—It was shown previously (Bistrzycki,

Abstr., 1901, i, 716) that benzilic acid condenses with phenols, and that the tertiary acids, formed readily on solution in concentrated sulphuric acid, lose carbon monoxide, forming carbinols. Diphenyleneglycollic acid likewise condenses with phenols, but the acids formed are only decomposed at high temperatures by concentrated sulphuric acid, and sulphonic acids of the expected carbinols are obtained.

9-p-*Hydroxyphenylfluorene*-9-*carboxylic acid*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C(CO_2H)\cdot C_6H_4\cdot OH$, prepared by condensation of diphenyleneglycollic acid with phenol, is obtained in microscopic, colourless, obliquely-cut plates from benzene containing a molecule of the solvent; it sinters and loses this at 98°, the residue becoming solid and getting red, m. p. 177° (decomp.). The benzene is difficult to remove; a preparation from alcohol had m. p. 178° (decomp.).

A by-product of the condensation is the *lactone* of 9-o-*hydroxyphenylfluorene*-9-*carboxylic acid*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!O\!<\!\begin{matrix}C_6H_4\\CO\end{matrix}\!>\!O$, which crystallises in microscopic, doubly refractive pyramids, m. p. 213°. On heating *p*-hydroxyphenylfluorenecarboxylic acid in a stream of air at 200°, carbon dioxide is eliminated, and 9-*p*-hydroxyphenylfluorene is formed, crystallising in colourless needles, m. p. 178—179° (decomp.), identical with the product obtained by Bistrzycki and Vlekke (*Diss.*, 1905) from phenol and fluorenyl alcohol.

9-p-*Acetoxyphenylfluorene*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CH\cdot C_6H_4\cdot OAc$, obtained on boiling *p*-hydroxyphenylfluorenecarboxylic acid with acetic anhydride, crystallises in slender needles, m. p. 139—140°.

9-p-*Hydroxy*-m-*tolylfluorene*-9-*carboxylic acid*, from diphenyleneglycollic acid and *o*-cresol, crystallises in matted prisms, m. p. 183—184° (decomp.). The corresponding *lactone* of 9-o-*hydroxy*-m-*tolylfluorene*-9-*carboxylic acid* separates in colourless plates, m. p. 147·5—149°.

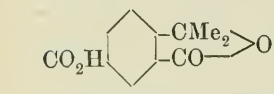
9-p-*Hydroxy*-m-*tolylfluorene*, obtained by heating the above carboxylic acid at 220°, crystallises in colourless, six-sided prisms, m. p. 165—166° (decomp.). The *acetate* crystallises in rosettes of colourless prisms, m. p. 95—97°.

Diphenyleneglycollic acid condenses with *m*-cresol, forming a *p*-hydroxy-acid, which crystallises with difficulty. At the same time, 9-o-*hydroxy*-p(?)-*tolylfluorene*-9-*carboxylic acid lactone* is obtained; it separates in aggregates of obliquely-cut prisms, m. p. 192°. The *lactone* of 9-(2′-*hydroxy*-5′-*tolyl*)*fluorene*-9-*carboxylic acid* is the only product of the condensation with *p*-cresol. It is at first obtained as a red oil, and crystallises in transparent plates with many faces, m. p. 138°.

9-p-*Methoxyphenylfluorene*-9-*carboxylic acid*, prepared by condensation with anisole, forms a crust of colourless, microscopic plates, m. p. 144—145° (decomp.). 9-p-*Methoxyphenylfluorene*, obtained on heating the foregoing compound at 160°, forms colourless prisms, m. p. 121—122°. E. F. A.

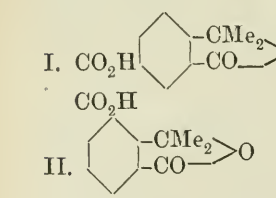
Synthesis of *iso*Propyl*iso*phthalic Acid and Dimethylphthalidecarboxylic Acid. Guido Bargellini (*Gazzetta*, 1910, 40, ii, 27—36).—The position assigned to the side-chain in santonin with respect to the ketonic group depends on the constitution of the dimethylphthalidecarboxylic acid obtained from it by Cannizzaro and Gucci (Abstr., 1893, i, 665). The acid has therefore been synthesised.

By nitrating cuminic acid with fuming nitric acid, 3-*nitrocuminic acid* (3-nitro-4-propylbenzoic acid) is obtained in prisms, m. p. 156—157°. Reduction with ammonium sulphide yields 3-*aminocuminic acid*, which crystallises in a labile modification, m. p. 104°, and a stable modification, m. p. 129°. Diazotisation, followed by heating with a solution of potassium copper cyanide, yields an uncrystallisable 3-cyanocuminic acid. This acid is very difficult to saponify, and it is necessary to convert it into the *amide*, $CO_2H\cdot C_6H_3Pr^{\beta}\cdot CO\cdot NH_2$, by boiling with sodium hydroxide. The product has m. p. 265°, and is converted into *iso*propyl*iso*phthalic acid by dissolving in concentrated sulphuric acid and adding sodium nitrite. The product crystallises from boiling water, and has m. p. 236°. Oxidation with potassium permanganate in alkaline solution converts it into dimethylphthalidecarboxylic acid (annexed formula), which is identical with that prepared from santonin.



C. H. D.

A New Synthesis of Dimethylphthalidecarboxylic Acid. Guido Bargellini and G. Forlì-Forti (*Gazzetta*, 1910, 40, ii, 74—89. Compare preceding abstract).—An attempt has been made to prepare the acid (II) for comparison with the acid obtained from santonin, which is assumed to have the constitution (I). The method selected was that of converting 3-nitrophthalic anhydride into the dimethylphthalide, and then of replacing the nitro-group by carboxyl. It is found, however, that the neighbourhood of the nitro-group prevents the anhydride from reacting with Grignard's reagent.



When dimethylphthalide is nitrated and the nitro-group replaced by carboxyl, an acid is obtained which is identical with that from santonin. The nitro-group is shown to occupy the para-position to the phthalide group, as it yields a nitrile which is readily saponified, whilst an *o*-nitrile would be difficult to saponify, as in the case of cyanocuminic acid. The nitration of methylphthalide (Giebe, Abstr., 1897, i, 63) and of diethylphthalide (Bauer, Abstr., 1904, i, 417; 1908, i, 274) is also known to yield para-derivatives. An attempt to prove the constitution directly by conversion into the hydroxy-compound, reduction, and distillation with lime, in order to examine the *iso*propylphenol produced, failed owing to the smallness of the yield obtained on reducing the hydroxyl compound with phosphorus and hydriodic acid.

The reduction of nitrodimethylphthalide with aluminium amalgam yields, instead of the amino-compound, an orange-yellow, crystalline

substance, m. p. 225—230°, devoid of basic properties. *5-Amino-dimethylphthalide*, $NH_2 \cdot C_6H_3 < \begin{matrix} CMe_2 \\ CO \end{matrix} > O$, obtained by reduction with stannous chloride, forms white leaflets, m. p. 117°. The *picrate* has m. p. 198—200°, softening at 192°. The *acetyl* derivative has m. p. 172—175°.

5-*Hydroxydimethylphthalide*, obtained by the diazo-reaction, forms white needles, m. p. 151—153°; its *acetyl* derivative has m. p. 76—78°; the *methyl ether* softens at 92—93° and melts at 98—99°.

In the attempt to prepare cyanodimethylphthalide by the diazo-reaction, an additive compound, m. p. 211—212°, is obtained, from which the compound may be isolated by heating in carbon dioxide, when cuminaldehyde volatilises, and a residue of 5-*cyanodimethyl-phthalide*, softening at 154° and melting at 159—160°, is obtained. Hydrolysis converts it into dimethylphthalidecarboxylic acid, identical with that obtained by other methods. C. H. D.

Retene. Paul Lux (*Monatsh.*, 1910, 31, 939—949. Compare Bucher, this vol., i, 239).—Methyl*iso*propyldiphenamide,

$$NH_2 \cdot CO \cdot C_6H_3Me \cdot C_6H_3Pr \cdot CO \cdot NH_2$$

(this vol., i, 239), crystallises from benzene, and has m. p. 204—206° (corr). When treated with bromine and potassium hydroxide solution, it yields 2 : 2′-*diamino*-3′-*methyl*-4-iso*propyldiphenyl*,

$$NH_2 \cdot C_6H_3Me \cdot C_6H_3Pr^{\beta} \cdot NH_2,$$

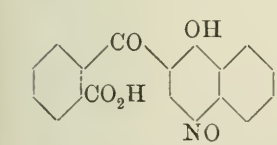
which forms colourless crystals, m. p. 89—90° (corr.). The *hydrochloride*, $C_{16}H_{20}N_2,2HCl$, melts above 240°. A better yield of the diamine can be obtained by using Jeffrey's method (Abstr., 1897, i, 315). The *urethane*, $CO_2Me \cdot NH \cdot C_6H_3Me \cdot C_6H_3Pr \cdot NH \cdot CO_2Me$, forms colourless crystals, m. p. 239—241° (decomp.), and when heated with slaked lime yields the diamine. It has not been found possible to diazotise the diamine and obtain the corresponding hydrocarbon; the product formed appears to be *methyl* iso*propylcarbazole*, $C_{16}H_{17}N$. It crystallises in glistening prisms, m. p. 124° (corr.), and yields a *picrate*, m. p. 166—167° (corr.).

3′-Methyl-4-*iso*propyldiphenamic acid,

$$NH_2 \cdot CO \cdot C_6H_3Me \cdot C_6H_3Pr \cdot CO \cdot OH,$$

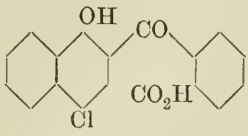
has m. p. 198—199°. J. J. S.

Preparation of *o*-4-Nitroso-1-hydroxynaphthoylbenzoic Acid. Anilinfarben- & Extrakt-Fabriken vorm. Joh. Rud. Geigy (D.R.-P. 223306).—o-4-*Nitroso*-1-*hydroxy*-*β*-*naphthoylbenzoic acid* (annexed formula) is prepared by treating finely-powdered *o*-1-hydroxy-*β*-naphthoylbenzoic acid with a concentrated solution of sodium nitrite, and keeping the paste well stirred at a temperature of 45° during six or eight hours, with further additions of water as necessary to keep it at a workable consistency. It forms sulphur-yellow crystals, m. p. 195° (the *sodium* salt is sparingly soluble), and on reduction yields *o*-4-amino-1-hydroxy-*β*-naphthoylbenzoic acid.



F. M. G. M.

Preparation of *o*-4-Chloro-1-hydroxy-β-naphthoylbenzoic Acid. Anilinfarben- & Extrakt-Fabriken vorm. Joh. Rud. Geigy (D.R.-P. 224538).—The action of ordinary chlorinating agents on *o*-1-hydroxy-β-naphthoylbenzoic acid is violent and leads to the formation of mixed products; it is now found that sulphuryl chloride in ethereal solution and at a low temperature gives a good yield of *4′-chloro-1′-hydroxy-β-naphthoyl-o-benzoic acid*, bright yellow prisms, m. p. 211°. F. M. G. M.



Action of Light on Benzaldehyde in the Presence of Iodine. Luigi Mascarelli (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 300—302. Compare this vol., i, 389, 561).—Among the products of this reaction, *iso*benzil, COPh·O·CPh:CPh·O·COPh, has now been identified. R. V. S.

Action of Light on *p*-Tolualdehyde in the Presence of Iodine. Luigi Mascarelli and G. Russi (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 239—242. Compare this vol., i, 389, 561).—The results obtained were similar to those already recorded in the case of benzaldehyde. The aldehyde when exposed to light in the presence of iodine for three years yielded (1) *p*-toluic acid; (2) a *trimeric tolualdehyde*, forming thin, colourless, prismatic crystals, m. p. 215°; (3) p-*tolyl* p-*toluate*, a pale yellow oil, b. p. 213—217°/15 mm., identical with that prepared by the Schotten-Baumann reaction (b. p. 224—228°/20—21 mm.). R. V. S.

Nature of the Catalytic Action of Zinc Chloride by the Condensation of Aromatic Ketones with Amines. G. Reddelien (*Ber.*, 1910, **43**, 2476—2480. Compare this vol., i, 118).—Benzophenone condenses readily with aniline and its derivatives in presence of anhydrous zinc chloride, or of the corresponding zinc chloride amine salt, for example, aniline zinc chloride, $ZnCl_2(NH_2Ph)_2$. When the amine forms no additive compound with zinc chloride (for example, *m*-nitroaniline, *m*-aminophenol), no condensation takes place. The zinc chloride amine compounds are not hygroscopic, and they act only as amine carriers, whereas the elimination of water from compounds, $OH·CR_2·NHR$, is brought about by the high temperature of the reaction. There is no interaction when benzophenone and aniline zinc chloride alone are heated at 160°, reaction immediately beginning when aniline is introduced. Benzophenoneanil is partly decomposed by zinc chloride at 160° with the formation of the compound $ZnCl_2(NH_2Ph)_2$.

The additive compounds of zinc chloride with the toluidines, xylidine, and phenylenediamine also act as catalysts. Anhydrous zinc chloride also acts as a condensing agent when more is used at a higher temperature, and the reaction is continued for a longer period. It acts not as a catalyst, but in withdrawing water.

On heating acetophenone with aniline in presence of zinc chloride, the chief product is triphenylbenzene, m. p. 170°. When zinc chloride

aniline is used, acetophenoneanil is obtained as a pale yellow oil, b. p. 198—200°/37 mm., solidifying to colourless crystals, m. p. 41°. It dissolves in concentrated sulphuric acid with an intense yellow coloration.

The following keto-imines have been condensed by means of zinc chloride amine or zinc chloride:

Bis-diphenylmethylene-p-phenylenediamine, $CPh_2{:}N{\cdot}C_6H_4{\cdot}N{:}CPh_2$, crystallises in golden-yellow, jagged plates, m. p. 180°. *p-Phenylenediamine zinc chloride*, $ZnCl_2,NH_2{\cdot}C_6H_4{\cdot}NH_2$, forms bunches of colourless, microscopic needles.

Fluorenoneanil, $C(C_6H_4)_2{:}NPh$, separates in golden-yellow needles grouped in rosettes, m. p. 89°. *Fluorenone-p-toluidine* forms lustrous, golden-yellow needles, m. p. 124°.

Diphenylenemethylene-p-aminophenol forms large, lustrous, dark brown plates, which become yellow on heating, m. p. 218—219°.

Bis-diphenylenemethylene-p-phenylenediamine crystallises in lustrous, red needles, m. p 278°. E. F. A.

Keto-anils. Max Busch and Ferd. Falco (*Ber.*, 1910, **43**, 2557—2564).—The easy production of keto-anils, $NR{:}CR'R''$, by the interaction of benzanilideimino-chloride and magnesium alkyl halogenides in ether (this vol., i, 729) led the authors to hope they had discovered a satisfactory method of testing the Hantzsch-Werner hypothesis of the stereoisomerism of tervalent nitrogen compounds (compare Straus and Ackermann, this vol., i, 241). *Deoxybenzoinanil*, $NPh{:}CPh{\cdot}CH_2Ph$, m. p. 89°, is ultimately obtained by the interaction of benzanilideimino-chloride and an excess of magnesium benzyl chloride; it forms slender needles and decomposes easily in alcoholic solution, especially by treatment with dilute sulphuric acid, into deoxybenzoin and aniline. When heated above 100° for two to three hours it is oxidised to a great extent to benzilanil; by exposing its solution in petroleum to sunlight for five to six hours, benzanilide and benzilanil are formed. (Equal molecular quantities of benzanilideimino-chloride and magnesium benzyl chloride react in ether ultimately to form chiefly diphenylbenzenylamidine.)

Phenyl α-naphthyl ketoneanil, $NPh{:}CPh{\cdot}C_{10}H_7$, obtained from the product of the reaction between magnesium α-naphthyl bromide and benzanilideimino-chloride in ether, exists in two forms: long, monoclinic leaflets, m. p. 101°, and triclinic prisms, m. p. 95°. The former are obtained from concentrated, the latter from dilute, solutions, and either can be obtained from a solution of the other by inoculation. Despite the difference of m. p. and of crystalline form, the two substances are regarded as dimorphous forms of an individual substance and not as stereoisomerides, because they are identical as regards colour, solubility, and chemical behaviour (*hydrochloride*, m. p. 187—188°; *picrate*, m. p. 165°). C. S.

***m-p*-Ditolyl Ketone.** James Lavaux and Maurice Lombard (*Bull. Soc. chim.*, 1910, [iv], 7, 913—915).—The action of methylene chloride on toluene in presence of aluminium chloride leads to the production of a mixture of hydrocarbons, which on oxidation furnishes

m-p-ditolyl ketone as one product. The ketone and some of its derivatives are described.

The yield of hydrocarbons in the condensation is about 60% of the theoretical, and the product consists of ditolylmethane and dimethylanthracene in the proportion 20 : 1. The ditolylmethane boils at 288—290°, and on oxidation with chromic acid in acetic acid furnishes *benzophenone*-3 : 4′-*dicarboxylic acid*, m. p. 337° (corr.), which crystallises from alcohol in small needles, and m-p-*ditolyl ketone*, m. p. 70·5°, which forms acicular crystals from boiling alcohol, and is readily soluble in organic solvents, particularly in chloroform; the *oxime*, m. p. 128—129°, forms needles, and the *semicarbazone*, m. p. 183° (approx.), crystallises from alcohol.

The constitution of the ketone is established by the fact that it yields on fusion with potassium hydroxide, *m*- and *p*-toluic acids, and the amides of these two acids on treatment with sodamide. T. A. H.

Reaction between *p*-Benzoquinone and Hydrogen Chloride. Arthur Michael and Philip H. Cobb (*J. pr. Chem.*, 1910, [ii], 82, 297—306).—The author takes exception to Thiele's and to Posner's explanation of the action of hydrogen chloride or bromide on *p*-benzoquinone by the theory of partial valency; this theory requires that halogenated quinols should be the first products of the reaction, whereas the author shows that in chloroform or carbon tetrachloride the initial product is quinhydrone or a mixture of quinhydrone and chloroquinone. C. S.

Mechanism of Quinone Reactions. Reply to Posner. Arthur Michael (*J. pr. Chem.*, 1910, [ii], 82, 306—321).—The author gives a further reply to Posner's criticisms (Abstr., 1904, i, 1029; 1909, i, 809) of his explanations of the reactions between *p*-benzoquinone and hydrogen chloride, aniline, and thiophenol (Abstr., 1904, ii, 164; 1909, i, 494). C. S.

Quinonoid Compounds. XXIII. Oxidation of Aniline. Richard Willstätter and Rikō Majima (*Ber.*, 1910, 43, 2588—2593).—A new example of ortho-condensation during the oxidation of aniline is furnished by the use of ferric chloride. A solution of aniline in 6% sulphuric acid is treated at 30° with a concentrated solution of ferric chloride (equiv. to $2\frac{1}{2}$O), whereby a mixture of aniline-black and dianilinobenzoquinone is produced, from which the latter may be isolated by sublimation in a vacuum, by extraction with boiling chloroform, or by extraction with nitrobenzene and sublimation at 15 mm. in carbon dioxide of the brown, crystalline product obtained from the cold solution. By reduction with tin and warm hydrochloric acid, dianilinobenzoquinone is converted into anilinoquinol, a solution of which in *N*-hydrochloric acid is oxidised by careful treatment with *N*/10-ferric chloride to *anilino*-p-*benzoquinone*,

$$O{:}C\!<\!\begin{matrix}C(NHPh){:}CH\\ CH{=}{=}{=}CH\end{matrix}\!>C{:}O,$$

m. p. 117—118°. This substance, which is much more intensely coloured than more complex anilinobenzoquinones, forms glistening,

bronze plates, which are brownish-yellow by transmitted light, gives intensely red solutions, is stable to sulphurous acid, and is reduced by zinc and acetic acid to dihydroxydiphenylamine.

An aqueous 2% solution of aniline is oxidised by Caro's method with saturated potassium persulphate in the presence of calcium carbonate; the red, crystalline product, m. p. 252°, which is regarded as *dianilino-p-benzoquinoneimine*, $NH:C<^{C(NHPh):CH}_{CH:C(NHPh)}>C:O$, yields dianilino-benzoquinoneanil with aniline and acetic acid, is very stable to lead dioxide and sulphuric acid, and dissolves in concentrated sulphuric acid with a brownish-violet colour, which turns violet by the addition of alcohol and warming. C. S.

Action of *p*-Benzoquinone on Diamines and Esters of Amino-acids. Wilhelm Siegmund (*J. pr. Chem.*, 1910, [ii], 82, 409—414. Compare Schlenk, Abstr., 1909, i, 807; Fischer and Schrader, this vol., i, 270).—By cooling a hot solution of *p*-benzoquinone (2 mols.) and diaminodiphenylmethane (1 mol.) in a little benzene, glistening, black, rhombic plates of a *substance*, $C_6H_4O_2,CH_2(C_6H_4\cdot NH_2)_2$, m. p. 72—73°, are obtained, which gives a violet coloration with concentrated sulphuric acid. In a similar way, *p*-benzoquinone and diaminostilbene yield brownish-black, metallic crystals of a *substance*,

$$3C_6H_4O_2,2C_2H_2(C_6N_4\cdot NH_2)_2,$$

m. p. 130°, which gives a yellow coloration with sulphuric acid. A benzene solution of *p*-benzoquinone and methyl *p*-aminobenzoate in the proportion 3 : 2 yields, after the addition of petroleum, dark red leaflets of the *substance*, $C_6H_4O_2,2NH_2\cdot C_6H_4\cdot CO_2Me$, m. p. 83°, which by prolonged boiling with *p*-benzoquinone in alcohol is converted into *methyl p-benzoquinone-2 : 5-diaminobenzoate*,

$$CO_2Me\cdot C_6H_4\cdot NH\cdot C<^{CO\cdot CH}_{CH\cdot CO}>C\cdot NH\cdot C_6H_4\cdot CO_2Me,$$

which crystallises in brown needles, and decomposes when heated. C. S.

Stable Primary Nitrosoamine. Gustav Heller and Apostolos Sourlis (*Ber.*, 1910, 43, 2581—2588).—4 : 6-Dinitroresorcinol (which forms a *diacetate*, m. p. 139°, and a *dibenzoate*, m. p. 343—344°) is suspended in glacial acetic acid and reduced by stannous chloride and 23% hydrochloric acid below 60°; by the addition of sodium acetate and acetic anhydride, the product of reduction is isolated as *6-nitro-4-acetylaminoresorcinol*, m. p. 261° (decomp.), which is hydrolysed by concentrated hydrochloric acid, yielding the *hydrochloride*, m. p. above 300°, of *6-nitro-4-aminoresorcinol*, m. p. 160—161° (decomp.). The reduction of 4 : 6-dinitroresorcinol by tin and hydrochloric acid and the treatment of the product with acetic anhydride yield *4 : 6-diacetyl-aminoresorcinol*, m. p. 335° (decomp.), which forms a *dibenzoate*, m. p. 214°.

6-Nitro-4-nitrosoamino-3-hydroxy-o-benzoquinoneoxime,

$$O:C<^{C(:NOH)\cdot C(OH)}_{C(NO_2)=\!=\!=CH}>C\cdot NH\cdot NO,$$

obtained from aqueous 6-nitro-4-aminoresorcinol hydrochloride or

hydrobromide and sodium nitrite (2 mols.) at 0°, forms dark yellow, hexagonal plates, and explodes when heated. The substance is regarded as a nitrosoamine, and not as an *anti*-diazohydroxide, because it does not react with acetyl chloride or acetic anhydride, and its solution in alcoholic hydrogen chloride does not combine directly with alkaline β-naphthol; its solution in concentrated hydrochloric acid is very stable, and the diazonium salt thereby produced combines at once with alkaline β-naphthol, forming 6-*nitro*-3-*hydroxy*-1 : 2-*quinoneoxime*-4-*azo*-β-*naphthol*. The substance shows the character of a quinoneoxime, a 1% solution in dilute acetone dyeing chromed wool a tobacco-brown colour; in faintly alkaline β-naphthol solution, the dyed wool acquires a distinct blue tinge. When the nitrosoamine in concentrated hydrochloric acid is treated with copper powder in the cold, the *hydrochloride*, $C_6H_3O_5N_2Cl,HCl$, m. p. 204—205°, of 4-*chloro*-6-*nitro*-3-*hydroxy*-1 : 2-*quinoneoxime*, yellow needles, m. p. 155°, is obtained, a 1% solution of which produces a clearer and yellower tone on chromed wool than the nitrosoamine. C. S.

Preparation of Acetylchloroaminoanthraquinones. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 224073).—Acetylchloroaminoanthraquinones, analogous to the phenyl compounds described by Bender (Abstr., 1887, 44), are readily obtained by the action of hypochlorous acid on an aqueous or dilute acetic acid solution or suspension of the required acetylaminoanthraquinone; if glacial acetic acid is employed, nuclear substituted derivatives are formed.

Acetylchloro-β-aminoanthraquinone is prepared by heating the components together on the water-bath until a permanent yellow colour is obtained; it forms small needles, somewhat soluble in nitrobenzene.

Acetylchloro-α-aminoanthraquinone requires greater excess of hypochlorous acid and more prolonged heating for its preparation.

These compounds are initial substances in the preparation of dyes. F. M. G. M.

Preparation of β-Anthraquinonylcarbimide from β-Aminoanthraquinone. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 224490).—*β-Anthraquinonylcarbimide*, m. p. 173°, is prepared by treating β-aminoanthraquinone with carbonyl chloride in nitrobenzene or xylene solution and keeping the mixture at the ordinary temperature until no red coloration is produced with dilute alcohol. The liquid is then heated to a temperature of 130—150°, when, on cooling, the product separates in colourless crystals. By treatment with moderately concentrated sulphuric acid, it is decomposed, yielding β-aminoanthraquinone with evolution of carbon dioxide. F. M. G. M.

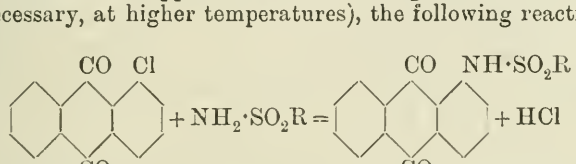
[Preparation of Aminoanthraquinone Thio-ethers.] Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 224589).—An account of the preparation of dyes obtained by the action of aliphatic mercaptans on negatively substituted anthraquinone derivatives (containing either halogen, nitro- or sulphonic groups) in aqueous

alkaline solution. The following compounds are mentioned: 1-*Amino*-4-*ethylthiolanthraquinone*, bronze prisms; 1-*benzoylamino*-4-*ethylthiol*-*anthraquinone*, bronze needles; 1-*acetylamino*-4-*ethylthiolanthraquinone*, red crystals; 1-*amino*-2 : 4-*diethylthiolanthraquinone*, red leaflets: 1 : 5-*diamino*-4 : 8-*diethylthiolanthraquinone*, steel-blue leaflets; *sodium* 1-*ethylthiolanthraquinone*-5-*sulphonate*, orange leaflets; 1 : 5-*diethylthiol*-*anthraquinone*, yellow leaflets; *sodium* 1 : 4-*diethylthiolanthraquinone*-8-*sulphonate*, red needles.

The colour of the solutions of these subtances in various solvents is tabulated in the patent. F. M. G. M.

[Preparation of Benzoylaminoanthraquinones.] Farben-fabriken vorm. Friedrich Bayer & Co. (D.R.-P. 225232).—A tabulated list of substituted benzoylamino- and dibenzoyldiamino-anthraquinones and their condensation products, with the colours of their solutions in pyridine, concentrated sulphuric acid, when dyed on wool, and in the vat. F. M. G. M.

Preparation of Arylsulphonaminoanthraquinones. Fritz Ullmann (D.R.-P. 224982).—When substituted halogen anthraquinones are heated with arylsulphonamides and potassium carbonate in the presence of copper acetate in boiling nitrobenzene solution (or, if necessary, at higher temperatures), the following reaction takes place:



1-p-*Toluenesulphonaminoanthraquinone*, long, yellow needles, m. p. 225°, was obtained from 1-chloroanthraquinone and *p*-toluenesulphonamide.

2-*Iodoanthraquinone*, needles, m. p. 170°, is prepared by the method described for 1-iodo-2-methylanthraquinone (Scholl, Abstr., 1907, i, 540), and when treated as above yielded 2-p-*toluenesulphonamino*-*anthraquinone*; this forms yellow needles.

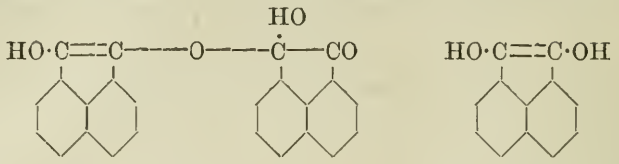
1 : 2-*Anthraquinonylsulphonaminoanthraquinone*, prepared from 1-chloroanthraquinone and *anthraquinone*-2-*sulphonamide*, is insoluble in the ordinary organic solvents, but dissolves in concentrated sulphuric acid, yielding a red solution.

1 : 5-*Dibenzenesulphonyldiaminoanthraquinone*, a yellow, crystalline powder, was obtained from 1 : 5-dichloroanthraquinone and benzenesulphonamide. F. M. G. M.

Preparation of Reduction Products of Acenaphthenequinones. Kalle & Co. (D.R.-P. 224979).—Reduction products from acenaphthenequinones have previously been studied; it is found that less energetic reduction, or the employment of milder reducing agents, gives rise to different products.

The *compound* (probably I) is produced by the action of alkaline

reducing agents; it forms yellow prisms, m. p. 248°, may be crystallised from tetrachloroethane, and yields a *hydrogen sulphite* and an *acetyl*



(I.) (II.)

derivative on treatment respectively with sodium hydrogen sulphite or acetic acid. The second *compound* (probably II) is obtained with acid, neutral, or alkaline reducing agents; it crystallises from alcohol in needles, has m. p. 254°, and forms two series of salts which are soluble in water. One alkali salt is pale blue, the other (when excess of alkali is employed) a deep violet blue; the *magnesium* salts are colourless. This substance can be acetylated, and combines with sodium hydrogen sulphite and with hydroxythionaphthens to form vat dyes.

F. M. G. M.

Preparation of Anthraquinone Derivatives. Kinzlberger & Co. (D.R.-P. 223210).—When anthraquinone is heated at 160° with sodium hydroxide and zinc dust (or other alkaline reducing agents) it yields a *dianthranol*, $C_{28}H_{18}O_2$, m. p. 230°. This on oxidation with alkaline potassium permanganate gives a *compound*, $C_{28}H_{16}O_2$, = $CO<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C{:}C<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CO$, forming yellow crystals, which turn green on pressure and blacken at 300° without fusion.

F. M. G. M.

Behaviour of Some Derivatives of Phenylhydroxylamine. Luigi Alessandri (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 122—129).—Additional reasons are adduced for the formula assigned (this vol., i, 552) to the product of the action of nitrosobenzene on safrole, which is identical with that obtained by the action of phenylhydroxylamine on methylenedioxycinnamaldehyde. The double linking between carbon atoms appears to be connected with the fact that the substance is coloured, since the analogous derivatives of benzaldehyde and phenylacetaldehyde are white. Moreover, *β-cyclo*citral yields a colourless derivative, so that the double linking in the above compound is probably in the side-chain. Benzoylacetaldehyde also yields a yellow derivative, although the constitution of the latter is not quite clear.

The *N*-phenyloximes described yield with hydroxylamine the corresponding oxime and phenylhydroxylamine, and they are rapidly affected by light. The action of light has been investigated further in the case of some analogous compounds. The cinnamaldehyde derivative, when exposed to light in sealed tubes freed from air, yields cinnamaldehyde and cinnamylideneaniline, CHPh:CH·CH:NPh. At the same time small quantities of other substances are formed, and an odour of *iso*nitrile is perceptible. The benzaldehyde derivative, when

exposed to sunlight and air, forms benzaldehyde, nitrosobenzene, and benzanilide (compare Ciamician and Silber, Abstr., 1905, i, 335), in addition to small quantities of azoxybenzene, *o*-hydroxyazobenzene, and dibenzaniline. Nitrosophenylhydroxylamine, O:NPh:N·OH, should form diazobenzene hydroxide analogously, and, in fact, an alkaline solution of it containing α-naphthol deposits benzeneazonaphthol when exposed to light. The process is rapid enough to have application in photography. The salts of the isomeric phenylnitroamines,

NPh:NO·OH,

are acted on similarly, but more slowly. The sodium derivative of nitrosophenylhydroxylamine yields nitrosobenzene rapidly in the light. Unsaturated nitro-derivatives, such as 7-nitrostilbene and piperonalnitroethane, are also decomposed by light.

When *β-cyclo*citral and phenylhydroxylamine are kept in a sealed tube in the dark for some days, N-*phenyl*-*β*-cyclo*citraloxime*, $C_{16}H_{21}ON$, is formed. It forms long, colourless needles, m. p. 109—110°. It is acted on by permanganate, nitrosobenzene being formed, and it is rapidly hydrolysed by dilute sulphuric acid. When it is exposed to light, it quickly resinifies, an odour of *cyclo*citral and *iso*nitrile is observed, and nitrosobenzene is formed. The last-named substance can be recognised by means of test-papers impregnated with hydroxylamine hydrochloride, sodium carbonate, and α-naphthol. *β*-cyclo*Citraloxime*, $C_{10}H_{17}ON$, prepared by the action of hydroxylamine on the above ether, or on *β-cyclo*citral, forms large, colourless rhomboidal crystals, m. p. 84°, has a characteristic odour, is volatile in steam, and is readily hydrolysed by acids. *β*-cyclo*Citralsemicarbazone*, $C_{11}H_{19}ON_3$, forms a felted mass of colourless needles, m. p. 209° (decomp.); Tiemann (Abstr., 1901, i, 158, 599) describes a semicarbazone, m. p. 166—167°. By the action of phenylhydroxylamine on benzoylacetaldehyde, a *substance*, $C_{15}H_{13}O_2N$, is obtained, crystallising in orange needles, m. p. 158° (decomp.), which when warmed with permanganate yields nitrosobenzene, but is stable towards light. R. V. S.

Nerol and Thymol in French Lavender Oil. F. Elze (*Chem. Zeit.*, 1910, **34**, 1029).—From a French lavender oil, having D^{15} 0·889, α_D −6°20′, and saponification number 99, a portion boiling at 85—100°/5 mm. was separated by distillation under reduced pressure. From this thymol was obtained by extraction with a dilute solution of sodium hydroxide, and from the residue nerol was isolated as the acid phthalate. T. A. H.

Molecular Rearrangements in the Camphor Series. III. Oxidation Products of *l*- and *d*-Laurolene. William A. Noyes and C. G. Derick (*J. Amer. Chem. Soc.*, 1910, **32**, 1061—1064. Compare Abstr., 1909, i, 133, 560).—Contrary to the authors' previous statements, the diketone obtained by oxidising *l*-laurolene does not undergo condensation readily. It has b. p. 204°/750 mm. (corr.); the optical activity varies with the method of preparation. The *disemicarbazone* has m. p. 194° (corr.), but the *dioxime* and *phenylhydrazone* are oily.

The rotation of *d*-laurolene varies with the method of preparation; a specimen prepared by the action of sodium nitrite on the hydro-

chloride of aminolauronic acid had $[\alpha]_D^{26\cdot2}$ 28·15°, whilst the density and b. p. were identical with that of the *l*-form. Oxidation with cold alkaline permanganate gave a *diketone*, $C_8H_{14}O_2$; the *disemicarbazone*, after melting at 192° (corr.), solidified, and then had m. p. 225° (corr.).

The properties of the oxidation products of laurolene are in accord with Eykman's representation of the structure of this substance (Abstr., 1907, i, 378). W. O. W.

Molecular Rearrangements in the Camphor Series. IV. Synthesis of Laurolene. William A. Noyes and L. P. Kyriakides (*J. Amer. Chem. Soc.*, 1910, **32**, 1064—1068. Compare preceding abstract).—The dimethyl*cyclo*pentanone obtained by heating *d*-αδ-dimethyladipic acid with lime is optically inactive. Grignard's reaction was applied to convert the product into 1 : 2 : 3-*trimethyl*cyclo*pentanol*, $C_8H_{16}O$, a liquid having b. p. 56—60°/8 mm., D_4^{15} 0·9121, $n^{16\cdot7}$ 1·4554. This substance loses water when heated, and is converted into laurolene; the transformation, however, is more easily effected by Zelinsky's method (Abstr., 1902, i, 2). The hydrocarbon thus prepared has b. p. 120—122°, $n^{16\cdot5}$ 1·4461, and on oxidation furnishes a diketone identical with that obtained from aminolauronic acid. The refractive index of synthetic laurolene is slightly less than that of the natural product, possibly through the presence of some ψ-laurolene.

The structure of laurolene as Δ^1-1 : 2 : 3-trimethyl*cyclo*pentene is, therefore, fully established. W. O. W.

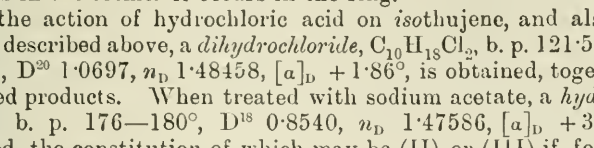
Molecular Rearrangements in the Camphor Series. V. Mechanism of the Reactions by which Laurolene is Formed. William A. Noyes (*J. Amer. Chem. Soc*, 1910, **32**, 1068—1070. Compare preceding abstracts).—A theoretical discussion. A methyl group is assumed to become detached and to unite with an adjacent carbon atom in the formation of laurolene from camphanic acid (Crossley and Renouf, Trans., 1906, **89**, 27) and from aminolauronic acid or anhydride. W. O. W.

Some Thujene Derivatives. Iwan L. Kondakoff and W. Skworzoff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 497—504. Compare Abstr., 1904, i, 438).—The authors consider that the structure of the compounds in the thujene series has not yet been satisfactorily settled. Thujene has never yet been obtained in a pure state, the product consisting of a mixture of dicyclic thujenes together with terpene and some other hydrocarbon. When the thujene obtained by the xanthate method is treated several times with 1% potassium permanganate, a tricyclic hydrocarbon or some stereoisomeric thujene was obtained, having b. p. 147·5—149·5°, D^{16} 0·8220, n_D 1·44809, $[\alpha]_D$ +109·09°.

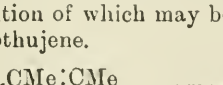
By removing hydrogen bromide from thujyl bromide, an unsaturated *alcohol* was obtained, b. p. 218—221°/760 mm., 96—100°/10 mm., D^{20} 0·9174, n_D 1·4793C, $[\alpha]_D$ +13·22°. Similarly, from the chloride, the *alcohol* obtained has b. p. 205—208°, D_4^{17} 0·8947, n_D 1·46128, $[\alpha]_D$ +23·22°. The taste and odour of both alcohols are alike, and similar to that of menthol and terpeneol. They do not yield urethanes, are largely converted into resins by the action of hydrochloric acid and

of succinic anhydride at 150°, are readily oxidised by concentrated potassium permanganate, and readily lose water. They are probably tertiary alcohols containing a five-membered ring, and are very similar to the alcohol obtained by Semmler from sabinene (Abstr., 1907, i, 145), excepting that in the latter the double bond is in the side-chain, whereas in the former it occurs in the ring.

By the action of hydrochloric acid on *iso*thujene, and also on the alcohol described above, a *dihydrochloride*, $C_{10}H_{18}Cl_2$, b. p. 121·5—125·5°/16 mm., D^{20} 1·0697, n_D 1·48458, $[\alpha]_D$ +1·86°, is obtained, together with resinised products. When treated with sodium acetate, a *hydrocarbon*, $C_{10}H_{16}$, b. p. 176—180°, D^{18} 0·8540, n_D 1·47586, $[\alpha]_D$ +3·11°, was obtained, the constitution of which may be (II) or (III) if formula (I) is taken as that of *iso*thujene.



(I.) (II.)



(III.)

Z. K.

Essential Oils. Roure-Bertrand Fils (*Sci. Ind. Bull. Roure-Bertrand Fils*, 1910, [iii], 1, 34—62).—[Justin Dupont and Louis Labaune.]—It has been shown previously that when cinnamyl alcohol in toluene is treated with hydrogen chloride at 100°, a chloride,

$$C_9H_9Cl,$$

is formed (this vol., i, 185). This is now shown to be cinnamyl chloride. On treatment with silver nitrate in alcohol, it yields a mixture of products, from which, by the action of sodium and subsequent fractional distillation, α-phenylallyl ethyl ether and cinnamyl ethyl ether were isolated. In addition, the mixture contains α-phenylallyl alcohol and cinnamyl alcohol (compare Charon, *Bull. Soc. chim.*, 1910, [iv], 7, 86). A good yield of the supposed linalyl chloride described already may be obtained by treating either linalool or geraniol in dry benzene with phosphorus trichloride (this vol., i, 184).

Hydrogen bromide reacts with geraniol or with *l*- or *d*-linalool, dissolved in toluene and maintained at 100°, to form a *bromide*, D^{15} 1·1450, $\alpha_D \pm 0$, n_D^{15} 1·507, b. p. 102—103°/6 mm., and this, when heated with potassium acetate in presence of toluene, yields linalyl acetate. When the bromide is treated with sodium ethoxide, it yields geranyl ethyl ether, b. p. 218°; with silver hydroxide, it gives linalool, and with silver nitrate, it furnishes linalool, geranyl ethyl ether, and possibly linalyl ethyl ether. In view of this complex reaction with silver nitrate, it is difficult to assign a constitutional formula to the bromide or the corresponding chloride.

Orange flowers collected in May and in October, 1909, yielded, by extraction with light petroleum, 736·3 and 663·6 grams respectively of total essential oil per 1000 kilos. of flowers. The May oil had D^{15} 0·8899, n_D^{15} 1·478, $\alpha_D = -0°48'$, acid value 0·7, saponification value 70·2, esters 24·6%, alcohols 51·0%, methyl anthranilate 3·53%. The

autumn oil had D^{15} 0·8887, n_D^{15} 1·476, $\alpha_D = -4°6'$, acid value 1·0, saponification value 95·8, esters 33·4%, alcohols 57·0%, methyl anthranilate 2·74%. These extracted oils differ from oil of neroli (distilled oil) in being lævorotatory, indicating that a change in rotation occurs as the result of distillation in steam. The higher yield of oil in May and the greater richness of this oil in methyl anthranilate is probably due to more active metabolism in the plant at that period and to the warmer temperature. Extracted orange flower oil usually contains over 7·0% of methyl anthranilate, and the low yield in these two samples may have been a result of the severe winter preceding the orange flower harvest of 1909. Analyses of the two oils, after removal of methyl anthranilate by Hesse and Zeitschel's process (Abstr., 1901, ii, 209), gave constants indicating that the May oil was poorer in combined and total alcohols than the October oil, the quantity of free alcohols being about the same; similarly, the October oil was richer in the primary alcohols, geraniol and nerol. It seems likely, therefore, that in May the flowers draw their supply of oil from the young branches, and in October from the older branches. The results also afford a further proof of the formation of terpene compounds in green organs.

Myrica Gale yielded, by steam distillation, 0·0443% of a greenish-yellow, volatile oil, having D^{25} 0·8984, α_D^{20} −5°16′, acid value 3·48, saponification value 17·98, esters 5·1%, total alcohols 14·4%, and free alcohols 10·5%. The oil exhibited a powerful purgative action, as did also a resin contained in the plant.

Java patchouli leaves furnished 0·803% of oil having D^{15} 0·9564, $\alpha_D = -28°8'$, saponification value 6·3, saponification value of acetylated oil 40·4.

Oil of *Mentha arvensis* var. *Javanica* had D^{15} 0·9979, $\alpha_D = +0°24'$, acid value 69·8, saponification value 49·7, saponification value after acetylation 153·3, corresponding with esters 17·5%, total menthol 48·2%, free menthol 34·4%, ketones or aldehydes, traces or none. The oil did not deposit crystals at −15°.

Ylang-ylang oil from Mayotte had D^{15} 0·9324, $\alpha_D = -47°40'$, acid value 1·0, saponification value 113·4, corresponding with esters 39·7%, total alcohols 41·0%, and free alcohols 9·8%.

An oil from French Guiana had D^{15} 0·8864, α_D −0°2′, total alcohols 71·3%, esters 5·8%, and dissolved to the extent of 80% in sodium hydrogen sulphite solution. The oil had a lemon-like odour, and was described as derived from *Andropogon Nardus*, L. The results indicated that it was derived from *A. citratus*, De Cand., and was abnormally rich in citronellal and geraniol.

In continuation of previous work (this vol., i, 401), Delépine finds that samphire oil contains dipentene, not limonene; in addition to the constituents already described, the oil contains traces of two phenols (one crystalline, and the other possessing an odour of cresote), and a small quantity of an alcohol having an odour of roses, with other indefinite products. T. A. H.

Essential Oils. Schimmel & Co. (*Bericht*, October, 1910).—The fruits of *Pimenta acris* from Mauritius yielded 3·3% of bright brown

oil, D^{15} 0·9893, α_D −1°20′, n_D^{20} 1·51902, eugenol 70% (compare *Bull. Imp. Inst.*, 1910, 8, 4).

Camphor oil from German East Africa had D^{15} 0·9203, α_D +39°42′, n_D^{20} 1·47753, and deposited camphor on cooling.

Cocking (*Chemist and Druggist*, 1910, 77, 19) has devised a method for detecting "Illurin balsam" in copaiba balsam, depending on the fact that if oil be distilled from these balsams in ten equal fractions, those from copaiba balsam show increasing laevorotation, whilst those from Illurin balsam show increasing dextrorotation.

Bergamot oil adulterated with ethyl citrate yields on evaporation to constant weight on the water-bath, a residue having a saponification value above that found for a similar residue from genuine oil, namely, 160, and the increase in the value may be used to obtain a rough indication of the extent of the adulteration. In the saponified product citric acid may be detected by means of calcium chloride or by Deniges' test (Abstr., 1899, ii, 454), the acid being first converted into acetonedicarboxylic acid by means of lead dioxide. Genuine bergamot oil contains only traces of citric acid, which, however, can be detected by Denigès' reaction. Genuine bergamot oil shows the same saponification value after heating at 100° during thirty or sixty minutes with *N*/2-potassium hydroxide in alcohol, but if terpinyl acetate is present the saponification value increases with longer heating, and in any case is higher than that shown by genuine oil. Glyceryl acetate may be detected by Jeancard and Satie's method, which depends on the partial extraction of the glyceryl acetate with water. For the detection and estimation of sophistication by esters of non-volatile acids, 1·5 to 2 grams of oil is treated in the ordinary way for the determination of the total saponification value [acid and ester values]. The saponified product is made distinctly alkaline, evaporated to dryness, the residue acidified with sulphuric acid, and the acid value of the distillate determined. The difference between the "total saponification value" and the "volatile acid value" for genuine oil is not more than 7. These methods are applicable also to lavender and "petit grain" oils.

In Rèunion geranium oil, linalool, α-terpineol, and phenylethyl alcohol were found in addition to traces of menthol and of an alcohol with an odour recalling that of borneol. Terpinenol may also be present.

Garlic contains according to Rindqvist (*Apoth. Zeit.*, 1910, 25, 105) a glucoside, *alliin*, which is decomposed by a specific enzyme, *allisin*, yielding garlic oil and lævulose.

A Chinese peppermint oil had D^{15} 0·9187, α_D −44°2′, ester value 43·9, total menthol 64·0%, and was soluble in 2·5 or more volumes of 70% alcohol.

Japanese peppermint oil contains Δ^1-menthenone, b. p. 235—237°/752 mm., D^{15} 0·9382, D^{20} 0·9343, α_D +1°30′, n_D^{20} 1·48411 (compare Wallach, Abstr., 1908, i, 812). The semicarbazone exists in the sparingly soluble α-form already described by Wallach (*loc. cit.*), and also in a readily soluble *β-form*, m. p. 171—172°. With hydroxylamine it forms an *oxime*, m. p. 107—109°, and an *oxamino-oxime*, m. p. 164—165°, which closely resembles the corresponding derivative of

carvenone, and must be constituted in an analogous manner, thus: $NH{\cdot}OH{\cdot}CMe<\begin{matrix}CH_2{\cdot}C(NOH)\\ CH_2\text{——}CH_2\end{matrix}>CHPr^{\beta}$. The ketone forms an unstable *dibromide*. With dehydrating agents, it yields *p*-cymene, and is oxidised by ferric chloride to thymol. Phosphorus pentachloride converts it into monochloroterpinene, and this on reduction with sodium in alcohol yields α-terpinene. On oxidation with permanganate the ketone furnishes formic acid, *α-hydroxy-α-methyl-δ'-isopropyladipic acid*, m. p. 143°, α-iso*propyl-γ-acetylbutyric acid* (the *semicarbazone* has m. p. 158—159°), and α-*iso*propylglutaric acid, the third acid resulting from further oxidation of the second, and the fourth in like manner from the third. These reactions can best be explained by the formula assigned to the ketone by Wallach (*loc. cit.*). For the characterisation of the ketone in essential oils, it is best isolated as the compound with sodium hydrogen sulphite, and identified by means of the α-semicarbazone. According to Murayama, Japanese peppermint oil also contains *l*-limonene (*J. Pharm. Chim.*, 1910, [vii], 1, 549).

A sage oil from Cyprus had D^{15} 0·9263, α_D −6°15′, n_D^{20} 1·46664, acid value 0, ester value 6·4, and acetyl ester value 36·0, and resembles Corfu sage oil.

From the first runnings of the distillation of sandalwood, the following constituents not previously observed have been isolated: (1)-Santenone, $C_9H_{14}O$, m. p. 58—61°, b. p. 193—195°, α_D −4°40′ in alcohol, is identical with the ketone prepared by Aschan (Abstr., 1908, i, 94) and by Semmler, and named by the latter π-norcamphor (Abstr., 1907, i, 1062); it yields a liquid *oxime*, b. p. 110—113°/6 mm., from which the ketone is not regenerated by warming with acids. (2) "Santenone alcohol," $C_9H_{16}O$, m. p. 58—62°, b. p. 196—198°, is apparently identical with Semmler's π-nor*iso*borneol (*loc. cit.*); on oxidation it yields santenone (π-norcamphor), furnishes a liquid *phenylurethane*, and is not etherified when warmed with alcohol and sulphuric acid. The isomeric alcohol (Aschan's santenol, *loc. cit.*; Semmler's π-norborneol, *loc. cit.*) on the contrary is etherified under these conditions, and yields, for example, *santenyl methyl ether*, $C_{10}H_{18}O$, b. p. 177—179°, D^{15} 0·9251, n_D^{20} 1·45841. It is suggested that Semmler's π-norborneol (Aschan's santenol) should now be called *iso*santenol and his π-nor*iso*borneol should be named santenol. (3) A *hydrocarbon*, $C_{11}H_{18}$, b. p. 183°, D^{15} 0·9133, D^{20} 0·9092, α_D −23°55′, n_D^{20} 1·47860, which may prove to be identical with Semmler's nor*tricyclo*eksantalane (Abstr., 1907, i, 432), since the latter, in view of Semmler's more recent work, must have the formula $C_{11}H_{18}$. (4) Nor-*tricyclo*eksantalal, $C_{11}H_{16}O$, b. p. 86—87°/6 mm., 222—224°/761 mm., D^{20} 0·9938, α_D −38°48′, n_D^{20} 1·48393, is identical with Semmler's product (this vol., i, 573). It yields a liquid *oxime*, b. p. 135—137°/7 mm., and on oxidation by air in dilute alkali furnishes the corresponding *acid*, m. p. 91—93°, α_D −33°17′ (in alcohol). On oxidation with permanganate, teresantalic acid is formed. The aldehyde can also be obtained from normal sandalwood oil. (5) Teresantalol, $C_{10}H_{16}O$, m. p. 112—114°, identical with Semmler and Bartlett's product (Abstr., 1907, i, 703) prepared from teresantalic acid. (6) *iso*Valeraldehyde.

Müller's santalone (Abstr., 1900, i, 678) was isolated by means of the semicarbazone. It occurs associated with an isomeric *ketone*, yielding a *semicarbazone*, m. p. 208—209°, and an *oxime*, m. p. 100° (approx.). The sesquiterpene portion of the oil was separated by fractional distillation into *α*-santalene, b. p. 118°/7 mm., 252°/753 mm., D^{15} 0·9132, α_D −3°34′, n_D^{15} 1·49205, and *β*-santalene, b. p. 125—126°/7 mm., D^{20} 0·8940, α_D −41°3′, n_D^{20} 1·49460 (compare Semmler, Abstr., 1907, i, 781). It is probable that pure *α*-santalene is slightly dextrorotatory. On hydration, *α*-santalene furnishes a tertiary alcohol, $C_{15}H_{26}O$, b. p. 154—157°/5—6 mm., D^{15} 0·9787, D^{20} 0·9753, n_D^{20} 1·51725, which has a cedar-like odour, and on treatment with formic acid loses water. The portion of the hydrocarbon recovered from the hydration process is different from the original material (compare von Soden and Müller, Abstr., 1899, i, 924).

Brassica juncea seed from India yielded an oil having D^{15} 0·9950, α_D +0°12′, n_D^{20} 1·51849, and soluble in 10 vols. of 70% alcohol. It boiled for the most part between 150—160° and 174—178°. The principal constituents were dimethyl sulphide, allyl cyanide, allylthiocarbimide (40%), and a *crotonylthiocarbamide* (50%), b. p. 175—176°, D^{15} 0·994, α_D +0°3′, n_D^{20} 1·52398, which furnished a *thiocarbamide*, m. p. 69—70°.

Juniper berry oil contains camphene (compare Abstr., 1909, i, 818).

Chamaecyparis Lawsoniana furnished 1% of citron-yellow oil, D^{15} 0·9308, α_D +23°48′, n_D^{20} 1·48844, acid value 3·7, ester value 61·6, acetyl ester value 78·8, containing some decaldehyde (?).

The leaves of *Cinnamomum glanduliferum* contained *d*-camphor. *Dacrydium Franklinii* wood yielded an oil, D^{15} 1·0443, α_D +0°6′, n_D^{20} 1·53287, containing much methyleugenol with some eugenol.

Eugenia apiculata leaves furnished 1·27% of brown oil, D^{15} 0·892, α_D +12°40′, n_D^{20} 1·47821, acid value 5·5, ester value 25·8, and acetyl ester value 65·3.

Perilla nankinensis leaf oil, D^{15} 0·9265, α_D −90°, n_D^{20} 1·49835, contains an *aldehyde*, b. p. 91°/4·5 mm., 104°/9 mm., 235—237°/750 mm., D^{20} 0·9645, D^{15} 0·9685, $[\alpha]_D$ −150·7°, n_D^{20} 1·50693, which yields an *oxime*, m. p. 102°, and a *phenylhydrazone*, m. p. 107·5°. The corresponding *acid* has m. p. 130°, and forms scaly crystals. A dextro-modification of the same aldehyde has been found in a "false camphor wood."

Thymbra spicata herb from Smyrna gave 1·5% of oil having an odour of thyme and containing 66% carvacrol. It had D^{15} 0·9460, α_D 0°, n_D^{20} 1·50675.

Xanthoxylum alatum fruits gave 3·7% citron-yellow oil, D^{15} 0·8653, α_D −23°35′, n_D^{20} 1·48131, and 0·9% of a crystalline, odourless substance, m. p. 83°, from which a small yield of a *benzoyl* derivative, m. p. 89°, was obtained. The oil appeared to consist mainly of hydrocarbons, and its odour recalled that of phellandrene.

Alpinia galanga oil is lemon-yellow, possesses a pungent, aromatic odour, and shows the following constants: D^{15} 0·9847, α_D +4°20′, n_D^{20} 1·51638, and contains, according to Ultée, pinene, cineol, camphor, and methyl cinnamate.

Gastrochilus pandurata oil resembles estragon and basil oils in odour,

and has D^{15} 0·8746, α_D +10°24′, n_D^{20} 1·48957, ester value 17·3, and is incompletely soluble in 10 vols. of 80% alcohol.

A résumé of recent work on the botany, pharmacology, analysis, and chemistry of essential oils is also given. T. A. H.

Cerebron. IV. Hermann Loening and Hans Thierfelder (*Zeitsch. physiol. Chem.*, 1910, 68, 464—470. Compare Abstr., 1907, i, 168).—Details are given of the preparation of cerebron from ox-brain, and the analysis of various fractions separated by extracting agents. The purest fraction was obtained in crystalline form, and contains C 69·19%, H 11·35%, and N 1·7%. The m. p. is 212—213°. Further work is promised on a second galactoside with which cerebron is usually mixed. W. D. H.

Effect of Alkali on Melanin. Ross Aiken Gortner (*J. Biol. Chem.*, 1910, 8, 341—363).—Alkali in small concentration readily destroys the greater portion of the melanin molecule, the nitrogen falling specially, whilst the carbon and oxygen percentages increase; the sulphur remains practically constant. If the concentration of alkali does not exceed 0·2%, a melanin is extracted from black wool, which is of constant composition, contains no ash, and is readily soluble in acids. W. D. H.

Synergin, the Prochomogen of the Respiration Pigment of Wheat Germs. Wladimir Palladin (*Biochem. Zeitsch.*, 1910, 27, 442—449).—The prochromogen of wheat, *synergin*, is decomposed by emulsin with production of a chromogen which is oxidised by peroxydase without addition of hydrogen peroxide. The prochromogen is extracted by ethyl and methyl alcohol, and is precipitated by acetone. It is not soluble in ether.

Taka-diastase, like emulsin, decomposes synergin with production of a chromogen which is oxidised by peroxydase. Pepsin is without action.

A number of substances were treated with emulsin and peroxydase in order to ascertain whether pigments are produced. Arbutin yielded a red coloration, less intense than that obtained with the chromogen from wheat, whilst the following compounds gave negative results: aesculetin, amygdalin, apiin, cholesterol, cratægin, cyclamin, digitalin, filicin, galactose, inositol, lecithin, phytin, quercitrin, raffinose, salicin, saligenin, solanine, syringin, and tyrosine.

Synergin is a phosphatide containing a carbohydrate group.

N. H. J. M.

Compounds of Acid Dyes with Various Organic Bases. Leopold Radlberger (*Zeitsch. physiol. Chem.*, 1910, 68, 391—394. Compare Abstr., 1908, i, 1001).—By mixing hot aqueous solutions of the components and cooling, the following insoluble or sparingly soluble salts have been obtained. Biguanide sulphate (which crystallises in large plates or in slender needles) yields the *salt*,

$$C_{34}H_{31}O_8N_9S_2,$$

with orange II, and $C_{24}H_{28}O_7N_{12}S_2$ with crystal-ponceau. Acetyl-

guanamine acetate yields an orange *salt*, $C_{20}H_{19}O_4N_7S,2H_2O$ (very hygroscopic when anhydrous), with orange II. C. S.

Causes of the Coloration of Animal Fibres. II. Wilhelm Suida (*Zeitsch. physiol. Chem.*, 1910, 68, 381—390. Compare Abstr., 1907, ii, 112).—Having shown that aqueous guanidine hydrochloride yields with picric acid and with crystal-ponceau sparingly soluble, crystalline precipitates, the filtrate containing in the first case all, in the latter 94·2%, of the chlorine, the author uses a reagent prepared by dissolving 5 grams of guanidine hydrochloride and 3 grams of acetic acid in 100 c.c. of water to test the acidity or basicity of a series of dyes which do not give in aqueous solution precipitates with acids alone. The results are: (i) all purely basic, non-sulphonated dyes do not give precipitates; (ii) in dyes which are aminosulphonic acids a decrease of precipitability frequently accompanies an increase in the number of amino- and of sulpho-groups; the generalisation, however, is not always trustworthy; (iii) nearly all of the hydroxyazo-dyes examined (with the exception of eosamine-*B* and azomagenta *G*), and also picric acid and alizarin-red, are more or less quantitatively precipitated, the quantitative course of the reaction being influenced by the number and the position of the hydroxyl and the sulpho-groups; (iv) the precipitation of hydroxy-dyes containing free or alkylated amino-groups is less the greater the number of amino-groups present; (v) whilst tartrazine does not give a precipitate, dyes containing hydroxyl and carboxyl groups, or these and sulpho-groups, give precipitates whether amino-groups are present or not; however, dyes which contain amino- (or alkylated amino-) and carboxyl, but no hydroxyl, groups do not yield precipitates. The outstanding result of the experiments is the important rôle played in the fixing of acid dyes by basic substances, by phenolic hydroxyl and aromatic amino-groups, the carboxyl and sulpho-groups exerting a quite subordinate influence.

Having shown that preliminary treatment of animal fibres with phosphotungstic acid retards the fixation of acidic dyes (*Zeitsch angew. Chem.*, 1909, 22, 2131), the author has examined the behaviour of the acid towards salts of guanidine. Any soluble salt of guanidine yields with phosphotungstic acid a white precipitate, which is easily soluble in ammonium hydroxide or carbonate; the precipitate remains colourless when boiled with a solution of an acidic dye, but instantly becomes coloured by the addition of a little ammonium hydroxide or carbonate, consequently experiments on guanidine in test-tubes follow quite the same course as those previously performed on animal fibres (*loc. cit.*). Since phosphotungstic acid is an excellent precipitant for the basic fission products of albumins, and since these products frequently contain the group NCN present in guanidine, there can be little doubt that the fixation of acidic dyes by albumins is due to these fission products or the NCN group contained therein; moreover, the chemical compounds formed by acidic dyes with animal fibres are probably constituted in stoichiometric proportions, since Radlberger has shown (Abstr., 1908, i, 1001) that the compounds of guanidine with acidic dyes are thus constituted.

An examination has been made of the behaviour of dyes towards

many substances related to the albumins or their fission products. The results are: (i) all aliphatic or cyclic substances containing the group :N·CO·N: or ·N:C(OH)·N:, such as carbamide, biuret, cyanuric acid, barbituric acid, alloxan, uric acid, theobromine, caffeine, phenylcarbamide, α-phenylhydantoin, glycine anhydride, phenylglycine anhydride, do not yield precipitates with acidic dyes; some of them possessing acidic character (barbituric acid, uric acid, cyanuric acid, ammelide, ammeline) form sparingly soluble compounds with basic dyes; (ii) all derivatives of guanidine with open chains which do not contain substituent acidic groups (aminoguanidine, dicyanodiamide, guanylcarbamide, biguanide, arginine) form sparingly soluble compounds with acidic dyes; (iii) all cyclic compounds containing the guanyl group give sparingly soluble or insoluble compounds with acidic dyes. It is noteworthy that most of the preceding substances which form insoluble or sparingly soluble compounds with acidic dyes are also precipitated by phosphotungstic acid. C. S.

Molecular Weight of Tannin. Leo F. Iljin (*J. pr. Chem.*, 1910, [ii], 82, 422—424).—The molecular weight of tannin, purified by the author's processes (Abstr., 1909, i, 503), has been determined by the ebullioscopic method in acetone in MacCoy's modification of Landsberger's apparatus; the values, varying between 1247 and 1637, confirm those of Sabanéeff and of Walden. The author is of opinion that crude tannin contains, in addition to digallic acid and Nierenstein's leucotannin, a not inconsiderable quantity of a complex derivative of gallic acid, for which the name "tannin" should be reserved. C. S.

δ-ω-Hydroxymethylfurfuraldehyde as the Cause of Some Colour Reactions of Hexoses. William Alberda van Ekenstein and Jan J. Blanksma (*Ber.*, 1910, 43, 2355—2361. Compare Abstr., 1909, i, 288; this vol., i, 461).—The compound previously described as β-hydroxy-δ-methylfurfuraldehyde is now shown to be the ω-hydroxy-compound, $O<\begin{matrix}C(CHO)=\!=\!=CH\\ C(CH_2\cdot OH):CH\end{matrix}$, as it can be obtained readily from chitose (Fischer and Andreæ, Abstr., 1903, i, 678), and when oxidised yields hydroxymethylpyromucic acid, $O<\begin{matrix}C(CO_2H)=CH\\ C(CH_2\cdot OH):CH\end{matrix}$ (compare Kiermayer, Abstr., 1896, i, 144), identical with the acid prepared by Fischer and Andreae (*loc. cit.*) and by Fenton and Gostling (Trans., 1899, 75, 429). J. J. S.

ω-Hydroxymethylfurfuraldehyde and its Relationship to Cellulose. Ernst Erdmann (*Ber.*, 1910, 43, 2391—2398).—ω-Hydroxymethylfurfuraldehyde (compare Alberda van Ekenstein and Blanksma, preceding abstract) can be prepared from Fenton and Gostling's crude ω-bromomethylfurfuraldehyde (Trans., 1901, 79, 361, 807) by shaking with aqueous alcoholic silver acetate and extracting with ether. It has b. p. 72°/0·002 mm., and the yield is 5·5 grams from 150 grams of filter paper. It has a pleasant odour, D_4^{23} 1·1022, and gives the usual aldehyde reactions. Its *semioxamazone*, $C_8H_9O_4N_3$,

forms colourless needles, m. p. 216°. When heated under pressure with oxalic acid solution at 134°, it yields an oil from which a *phenylhydrazone*, m. p. 137°, has been isolated. The same phenylhydrazone can be obtained from the oil, b. p. 110°/0·002 mm., formed as a by-product in the preparation of the ω-hydroxymethyl compound. It is suggested that this oil, b. p. 110°/0·002 mm., is identical with the product obtained by Kiermayer from sucrose (Abstr., 1896, i, 144). Its semioxazone is not molten at 260°. J. J. S.

Action of Methyl Sulphate on Dimethylpyrone. Adolf von Baeyer (*Ber.*, 1910, **43**, 2337—2343).—Kehrmann and Duttenhöfer's dimethylpyrone methiodide (Abstr., 1906, i, 447) is shown to have the formula $I\cdot O\langle\begin{matrix}CMe\cdot CH\\CMe:CH\end{matrix}\rangle C\cdot OMe$.

The parent substance, $I\cdot O\langle\begin{matrix}CH\cdot CH\\CH:CH\end{matrix}\rangle CH$, is termed pyroxonium iodide.

Dimethyl-p-methoxypyroxonium perchlorate, $OMe\cdot C_5H_2Me_2O\cdot ClO_4$, is obtained when dimethylpyrone and methyl sulphate are heated at 50° until the mixture becomes orange-coloured, and the cold product is treated with 20% perchloric acid solution. It is also formed by the action of perchloric acid solution on Kehrmann and Duttenhöfer's iodide. It crystallises from methyl alcohol, is sparingly soluble in cold water, and is resolved into its components when boiled with water for some time. An aqueous solution of ammonium carbonate converts the perchlorate or the iodide into 4-methoxylutidine, the picrate of which melts at 154°, and a solution of sodium acetate or water and magnesium carbonate react with the perchlorate, yielding the *methyl ether* of the enolic form of diacetylacetone, $CH_2Ac\cdot C(OMe):CHAc$, as a colourless oil. J. J. S.

Preparation of Coumarin. Fritz Raschig (D.R.-P. 223684).—The synthetical production of coumarin has been checked by the cost of the salicylaldehyde employed in the usual method of preparation; it is found that this can be replaced by an *o*-tolyl ester containing two atoms of chlorine in the side-chain.

Di-ω-chlorotolyl phosphate (obtained by treating *o*-tolyl phosphate with chlorine at 160—180°) is mixed with anhydrous sodium acetate and heated at about 180° during six hours; the temperature is then raised to 220°, when pure coumarin distils and solidifies in the receiver. The phosphoric acid can be replaced by other acids.

F. M. G. M.

Constitution of α-Pyrocresol. Franz Zmerzlikar (*Monatsh.*, 1910, **31**, 897—902. Compare Schwarz, Abstr., 1883, 204; Bott, *J.C.S.I.*, 1887, **6**, 646; Bott and Miller, Trans., 1889, **55**, 51).—When α-pyrocresol oxide is fused with potassium hydroxide, the products are *m*-hydroxy-*p*-toluic acid ($Me:OH:CO_2H = 1:3:4$), *m*-hydroxyterephthalic acid, and *m*-cresol.

The formation of these compounds is readily acccounted for on the assumption that α-pyrocresol oxide is 4:2′- or 4:4′-dimethylxanthone,

$C_6H_3Me<^{O-}_{CO}>C_6H_3Me$; α-pyrocresol itself would then be the corresponding dimethylxanthan, $C_6H_3Me<^{O-}_{CH_2}>C_6H_3Me$. The identity of synthetical 4 : 4′-dimethylxanthone (Weber, Abstr., 1892, 1093) with α-pyrocresol oxide has been proved, and hence α-pyrocresol is 4 : 4′-dimethylxanthan. J. J. S.

Preparation of Phenoxozone. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 223367).—The preparation of phenoxozone, m. p. 118—119°, has previously been described (Ullmann and Stein, Abstr., 1906, i, 258); it is now found that it can be prepared in 74% yield by gradually heating sodium *o*-chlorophenoxide to 220° in an iron retort, and subsequently distilling under a pressure of 20—30 mm. F. M. G. M.

Preparation of Thionaphthen Derivatives from Arylthiolacetic Acids and their Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 224567).—When arylthiolacetic acids of the type $R{\cdot}S{\cdot}CH_2{\cdot}CO_2R^1$ (where R is a simple or substituted benzene ring, or naphthalene residue, and R^1 hydrogen, a metal, alkyl, or aryl group) are treated with such reagents as phosphoric oxide, zinc, or aluminium chlorides, chlorosulphonic acid, or anhydrous oxalic acid, the following inner condensation take place:

$$S<^{CH_2}_{R}>CO{\cdot}OR \longrightarrow S<^{CH}_{R}>C{\cdot}OH.$$

This reaction has only been studied previously with phenyl-, *o*- and *p*-tolyl-, and *p*-bromophenyl-thiolacetic acids, but has now been extended to naphthalene derivatives; the products when pure are colourless compounds soluble in alkali, and yielding vat dyes on oxidation.

2-*Hydroxy*-4-*methylthionaphthen* is prepared by heating ethyl *p*-tolylthiolacetate (obtained from thio-*p*-cresol and ethyl chloroacetate) with phosphoric oxide at 100—150°, and separating the product by distillation in steam; it forms long, colourless needles, m. p. 103°.

4-*Chloro*-2-*hydroxythionaphthen*, colourless needles, m. p. 100°, is similarly prepared from *p*-chlorophenylthiolacetic acid (m. p. 107°).

The *compound*, obtained from sodium α-naphthylthiolacetate, when treated with chlorosulphonic acid at 0—5° is yellow, and not volatile in steam. F. M. G. M.

Substituted Rhodanines and their Condensation Products with Aldehydes. IX. Oskar Antulich (*Monatsh.*, 1910, **31**, 891—895).—Ammonium *p*-anisylidenedithiocarbamate, prepared by Losanitsch's method (Abstr., 1907, i, 693), reacts with ethyl chloroacetate, yielding p-*anisidylrhodanine*, $OMe{\cdot}C_6H_4{\cdot}N<^{CS{\cdot}S}_{CO{\cdot}CH_2}$, which crystallises from alcohol in yellow plates, m. p. 153°. The following condensation products have been obtained by the action of a glacial acetic acid solution of an aromatic aldehyde on the rhodanine.

1-p-*Anisidyl*-3-*benzylidenerhodanine*, $OMe{\cdot}C_6H_4{\cdot}N<^{CS{\cdot}S}_{CO}>C{:}CHPh$,

lemon-yellow prisms, m. p. 190°; 1-p-*anisidyl*-3-m-*nitrobenzylidene-rhodanine*, $C_{17}H_{12}O_4N_2S_2$, a chrome-yellow, crystalline powder; 1-p-*anisidyl*-3-p-*hydroxybenzylidenerhodanine*, $C_{17}H_{13}O_3NS_2$, yellow needles from acetone, m. p. 258°; 1-p-*anisidyl*-3-p-*dimethylaminobenzylidene-rhodanine*, $OMe\cdot C_6H_4\cdot N<^{CS\cdot S}_{CO-}>C:CH\cdot C_6H_4\cdot NMe_2$, orange-red plates, m. p. 219°, and 1-p-*anisidyl*-3-p-*hydroxy*-m-*methoxybenzylidenerhodanine*, $C_{18}H_{15}O_4NS_2$, pale orange-coloured, crystalline powder, m. p. 210°.

J. J. S.

Preparation of Formyl Derivatives of Morphine Alkaloids. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 222920).—The formyl derivatives of the morphine alkaloids are readily obtained by heating either the bases, their salts, or halogen compounds with formic acid or sodium formate, the alcoholic hydroxyl of the base being the point of attack.

Formylcodeine, colourless crystals, m. p. 180°, is prepared by boiling dry codeine with an excess of formic acid (100%) during five or six hours; it is insoluble in water, and sparingly so in alcohol and ether.

Formylmorphine is obtained by boiling together dry morphine hydrochloride (10 parts), sodium formate (5 parts), and formic acid (50 parts). It has m. p. 220° (about), and at 253° decomposes into its progenitors; the *salts* are crystalline. The formyl derivatives of morphine ether and of methylmorphinemethine can be similarly prepared.

F. M. G. M.

Preparation of Morphine Esters of Acylaromatic Hydroxycarboxylic Acids. J. D. Riedel (D.R.-P. 224197).—When morphine is treated with the acid chlorides of acylphenolcarboxylic acids, compounds of the type $C_{17}H_{18}O_2N\cdot OCO\cdot R\cdot OR'$ (R = an arylene, R' = an acyl) and of great therapeutic value are produced.

p-*Acetoxybenzoylmorphine*, $C_{26}H_{25}O_6N$, long, prismatic needles sintering at 225°, m. p. 232° (with decomp.), was prepared as follows: p-*Acetoxybenzoic* acid, m. p. 196°, obtained from *p*-hydroxybenzoic acid and acetic anhydride, was treated with phosphorus pentachloride and the mixture distilled in a vacuum, yielding p-*acetoxybenzoyl chloride*, which after distillation at 161—162°/12 mm. solidified to long needles, m. p. 30°. This chloride (dissolved in chloroform) was slowly shaken with morphine in aqueous alkaline solution, the liquids separated, and the product obtained in crystalline form by the addition of ethyl-acetate. The *methochloride*, small prisms, was obtained by the action of methyl sulphate and sodium chloride on the base.

p-*Methyl-carbonatobenzoylmorphine*, $C_{26}H_{25}O_7N$, was analogously prepared from *p*-methyl-carbonatobenzoyl chloride (Fischer, Abstr., 1908, **94**, i, 892); it forms colourless needles, m. p. 175—176° (with decomp.). The *hydrochloride* crystallises from either methyl or ethyl alcohol in large prisms containing one molecule of the respective alcohol of crystallisation, and with m. p. 165—190° (indefinite). When shaken with the requisite quantity of dilute alcoholic ammonia and kept at the ordinary temperature, the *p*-methyl-carbonato-group is eliminated, and p-*hydroxybenzoylmorphine*, $C_{24}H_{23}O_5N$, m. p. 230—237° (with

decomp.), separates out; the *hydrochloride* forms prismatic needles; the *methobromide*, small leaflets, was prepared by the action of methyl sulphate and potassium bromide in chloroform solution.

F. M. G. M.

Preparation of Halogenhydroxyalkyl-substituted Xanthine Bases. Chemische Werke vorm. Dr. Heinrich Byk (D.R.-P. 224159).—When xanthine bases are treated with substituted halogen alkyloxides, reaction occurs with the iminic hydrogen.

Chlorohydroxypropyltheophylline,

$$\begin{array}{l} NMe\cdot CO\cdot C\text{—}N\cdot CH_2\cdot CH(OH)\cdot CH_2Cl, \\ CO\cdot NMe\cdot C\cdot N{:}CH \end{array}$$

m. p. 141—143°, is prepared by heating theophylline with epichlorohydrin in a closed vessel at 130° during several hours with continual stirring; it is readily soluble in water, and when boiled with an alkaline hydroxide is converted into dihydroxypropyltheophylline.

F. M. G. M.

Strychnine Alkaloids. IX. Derivatives of Strychninesulphonic Acid I. and Oxidation of Bromostrychnine. Hermann Leuchs and Paul Boll (*Ber.*, 1910, 43, 2362—2374. Compare Abstr., 1909, i, 120, 671).—The sulphonic acid group of strychninesulphonic acid is not attached to one of the benzene nuclei, and hence the acid readily yields substitution products, for example, mono- and di-chloro-derivatives, a monobromo-, a nitro- and a nitrobromo-derivative. Strychnine itself yields a hydrate of a dinitro-derivative, and it is probable that one of the nitro-groups of this derivative occupies the same position as the sulphonic group in strychninesulphonic acid. The nitrosulphonic acid is readily reduced to the corresponding amino-acid, and with alkaline reducing agents, azostrychninesulphonic acid is also formed. So far it has not been found possible to prepare diazo- and hydroxy-compounds corresponding with the amino-derivative. The sulphonic acid group of strychninesulphonic acid is not removed by heating with concentrated hydrochloric acid, but an atom of chlorine is introduced: $C_{21}H_{22}O_5N_2S + HCl = C_{21}H_{21}O_4N_2SCl + H_2O$, and this chloro-acid when boiled with water loses hydrogen chloride, yielding a product isomeric with the original sulphonic acid and termed *iso*strychninesulphonic acid I. The authors do not agree with the conclusion that the bromine atom in bromostrychnine is attached to a carbon atom of a side-chain (Abstr., 1885, 911; Ciusa and Scagliarina, this vol., i, 583.)

Nitrostrychninesulphonic acid I., $C_{21}H_{21}O_7N_3S$, prepared by boiling the base for a short time with 5*N*-nitric acid in the presence of carbamide, crystallises in massive, straw-yellow prisms, which are not molten at 300°. It has $[\alpha]_D^{20}$ −364° in dilute sodium hydroxide solution. The corresponding *amino*-acid, $C_{21}H_{23}O_5N_3S$, crystallises in colourless needles or thin plates, and decomposes at 270°. Its solution in sodium hydroxide has $[\alpha]_D^{20}$ −244·8°. The *hydrochloride*,

$$C_{21}H_{23}O_5N_3S,HCl,$$

and sulphate are readily soluble, but the nitrate sparingly soluble. *Azostrychninesulphonic acid I.*, $C_{42}H_{42}O_{10}N_6S_2$, crystallises in orange-

yellow plates containing $8H_2O$, and when dehydrated under reduced pressure at 80° forms greenish-yellow crystals.

Bromostrychninesulphonic acid I., $C_{21}H_{21}O_5N_2SBr$, prepared by the action of a solution of bromine in hydrobromic acid (D 1·46) on the sulphonic acid, forms colourless, rectangular prisms or plates. In aqueous sodium hydroxide solution it has $[\alpha]_D^{20}$ −233·6°.

Bromonitrostrychninesulphonic acid, $C_{21}H_{20}O_7N_3SBr,H_2O$, formed by the action of bromine on the nitro-acid, crystallises in broad, yellow needles. Care is required in the preparation, as there is a tendency for the bromine to replace the nitro-group.

Chlorostrychninesulphonic acid I., $C_{21}H_{21}O_5N_2SCl,H_2O$, is formed by the action of chlorine water and concentrated hydrochloric acid on the sulphonic acid at 0°, and crystallises in massive, six-sided prisms with $[\alpha]_D^{20}$ −239·9°. *Dichlorostrychninesulphonic acid I.*,

$$C_{21}H_{20}O_5N_2SCl_2,H_2O,$$

forms six-sided plates and has $[\alpha]_D^{20}$ −155·9°.

Chloride of iso*strychninesulphonic anhydride*, $C_{21}H_{21}O_4N_2SCl,2H_2O$, obtained by the action of concentrated hydrochloric acid on the sulphonic acid at 130—135°, crystallises in long prisms, loses its water of hydration at 80° under reduced pressure, and gives Otto's strychnine reaction. iso*Strychninesulphonic acid I*, $C_{21}H_{22}O_5N_2S,2H_2O$, has $[\alpha]_D^{20}$ −242° to −244° in alkaline solution, and is not so readily soluble in water as the isomeric acid. The *chloride* of iso*nitrostrychninesulphonic anhydride I.*, $C_{21}H_{20}O_6N_3SCl$, crystallises in irregular plates, practically insoluble in water, and iso*nitrostrychninesulphonic acid I.*, $C_{21}H_{21}O_7N_3S$, has $[\alpha]_D^{20}$ −285·9°, and its solubility in water is 1 in 2000.

When oxidised with hydrogen peroxide, the sulphonic acid I. yields the *amino-oxide*, $C_{21}H_{22}O_6N_2S,2H_2O$, in the form of long, colourless needles, with $[\alpha]_D^{20}$ −101·8° in alkaline solution. It is readily reduced by sulphurous acid. The nitrosulphonic acid I. when oxidised in a similar manner yields the *amino-oxide*, $C_{21}H_{21}O_8N_3S$, as massive, yellow needles, with $[\alpha]_D^{20}$ −240°.

Bromostrychninonic acid, $C_{21}H_{19}O_6N_2Br$, prepared by oxidising bromostrychnine (Beckurts, Abstr., 1890, 1329) in acetone solution with permanganate, crystallises in twinned needles, is hydrated, has m. p. 274—276° (corr.), and $[\alpha]_D^{20}$ −54·8° in alkaline solution. J. J. S.

Strychnine Alkaloids. X. Reactions of Strychninonic Acid and of Strychninolone. Hermann Leuchs and Paul Reich (*Ber.*, 1910, **43**, 2417—2429. Compare Abstr., 1908, i, 564; 1909, i, 602). —Attempts have been made to prove the presence of two carboxylic groups in strychninonic acid. With methyl alcohol and hydrogen chloride a monomethyl ester is formed, and ultimately products containing chlorine, and these with sodium carbonate yield two substances, one containing two carbomethoxy-groups and the other a carboxylic and a carbomethoxy-group, but both derived from the original acid plus a molecule of water, so that it is possible that the second carboxylic group is formed by the addition of water to an :N·CO· group in the original strychninonic acid molecule.

The acid reacts with dilute hydrochloric acid, yielding two hydrates containing respectively one and two molecules of water. The former

is regarded as an imino-acid formed by the rupture of the $\begin{matrix}:N\\ \\ \cdot CO\end{matrix}$ group. In the other, the second molecule of water is probably attached to the carbonyl group.

An anilide is formed when the acid is boiled with aniline, and hence the carbonyl group is in all probability not in the α-position with respect to the carboxylic group.

Methyl strychninonate, $C_{22}H_{22}O_6N_2$, crystallises from methyl alcohol in brilliant prisms, m. p. 247—249°. A *hydrate* of the methyl ester, $C_{22}H_{24}O_7N_2$, is formed when the solution in methyl alcohol is saturated with hydrogen chloride, and crystallises in rectangular prisms or plates, m. p. 184—186°. It dissolves in both dilute acids and dilute alkalis. The *dimethyl ester hydrate* forms a platinichloride, probably $C_{46}H_{54}O_{14}N_4PtCl_6$.

Strychninonic acid hydrate, $C_{21}H_{22}O_7N_2$, crystallises from water in long needles containing $2H_2O$, which it loses at 105°, and then has m. p. 270—275° (decomp.). It has $[\alpha]_D^{20}$ +39·6°. The *dihydrate*,

$$C_{21}H_{24}O_8N_2,H_2O,$$

is less soluble in water, and crystallises at 0° in rectangular prisms; it has m. p. 235—240°. It yields a *sodium* salt, $C_{21}H_{23}O_8N_2Na$, which forms small prisms, m. p. 250—255° (decomp.).

Nitrostrychninonic acid, $C_{21}H_{19}O_8N_3$, obtained by the action of 5*N*-nitric acid and carbamide on strychninonic acid and extracting with chloroform, crystallises from glacial acetic acid in six-sided plates, m. p. 264—266° (decomp.). Yield, 20—25%.

Strychninonanilide, $C_{27}H_{25}O_5N_3$, crystallises from 75% acetic acid in short, massive prisms, m. p. 255° (decomp.).

Strychninolone contains a hydroxyl group, and yields an *acetyl* derivative, $C_{21}H_{20}O_4N_2$, which crystallises from methyl alcohol in brilliant prisms, m. p. 126—128° (decomp.). With a chloroform solution of phosphoryl chloride, strychninolone yields *strychninolone chloride hydrate*, $C_{19}H_{19}O_3N_2Cl$, which crystallises from absolute alcohol in slender needles, m. p. 236°.

When heated with concentrated hydrochloric acid at 100°, strychninolone yields two hydrates. The *hydrochloride* of *hydrate I*,

$$C_{19}H_{21}O_4N_2Cl,$$

crystallises from hot water in glistening prisms, m. p. 305—310° (decomp.). The hydrate itself is a syrup. The *hydrate II*,

$$C_{19}H_{20}O_4N_2,4H_2O,$$

crystallises from water in thick prisms or long needles, m. p. 239—240°. Both hydrates have the properties of amino-acids.

J. J. S.

Glutamic Acid and Pyrrolidonecarboxylic Acid. Emil Abderhalden and Karl Kautzsch (*Zeitsch. physiol. Chem.*, 1910, **68**, 487—503. Compare this vol., i, 230).—Owing to the ease with which it changes into glutamic acid, the formation of pyrrolidonecarboxylic (not pyrrolidinecarboxylic, *loc. cit.*) acid has not yet been detected amongst the products of the hydrolysis of albumins by the ordinary processes. With this end in view, the authors have instituted further experiments for the separation of pyrrolidonecarboxylic acid from

other amino-acids, especially from glutamic acid. Utilising the amino-group in the latter, the authors have converted it by means of ethyl chloroformate into *carbethoxyglutamic acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO_2Et,$$

which forms a *barium* salt, $C_8H_{11}O_6NBa,H_2O$, a *silver* salt,

$$C_8H_{11}O_6NAg_2,$$

and an amorphous, green *copper* salt, $C_8H_{11}O_6NCu$, which is much less soluble in water than copper pyrrolidonecarboxylate. It is noteworthy that glutamic acid, owing to the influence of the amino-group on the neighbouring carboxyl, behaves generally like a monobasic acid (*loc. cit.*), whereas carbethoxyglutamic acid exerts its dibasic function in salt formation. The separation of glutamic acid from pyrrolidonecarboxylic acid is very conveniently effected by Siegfried's carbamino-reaction (Abstr., 1906, i, 144).

The formation of pyrrolidonecarboxylic acid from glutamic acid by heating has been examined more thoroughly. At 150—160°, *d*-glutamic acid yields a product, m. p. about 145°, $[\alpha]_D$ −10·06° in water, from which *l*-pyrrolidonecarboxylic acid, $[\alpha]_D$ −11·5°, can be separated by fractional crystallisation from water. At 180—220°, *d*-glutamic acid yields chiefly *i*-pyrrolidonecarboxylic acid. At 160—170°, under conditions as yet unknown, *d*-glutamic acid yields occasionally a small quantity of a *substance*, $C_5H_7O_3N$, m. p. 180—182°, $[\alpha]_D$ +4·24° in water. A *l*-pyrrolidonecarboxylic acid, obtained from *d*-glutamic acid and having $[\alpha]_D$ −11·27° in water, had $[\alpha]_D$ +4·24° in methyl alcohol and +3·75° in ethyl alcohol. A *l*-pyrrolidonecarboxylic acid, $[\alpha]_D$ −9·38° (therefore containing about 19% of the inactive acid), was treated with 5*N*-hydrochloric acid for six to seven days, whereby *d*-glutamic acid, $[\alpha]_D$ 23·3°, was obtained; pure *d*-glutamic acid in 5*N*-hydrochloric acid has $[\alpha]_D$ +28·88°. Under similar conditions, *i*-pyrrolidonecarboxylic acid yielded *i*-glutamic acid hydrochloride, m. p. 200°.

Silver glutamate, $C_5H_7O_4NAg_2$, *basic zinc glutamate*,

$$(C_5H_8O_4N)_2Zn,ZnO,$$

and the *lead*, *copper*, and *silver* salts of pyrrolidonecarboxylic acid are described. C. S.

Existence of Liquid Racemic Compounds. Albert Ladenburg and Sobecki (*Ber.*, 1910, 43, 2374—2380).—The freezing-point curve of mixtures of *d*- and *l*-pipecolines has been determined; the curve shows two eutectics at −6·65° and a maximum at −4·9°, corresponding with the formation of a definite racemic compound.

The solubility of dipentene in 98·99% acetic acid at 12° has been determined, the method of estimation being conversion into bromide. The saturated solution of dipentene in acetic acid when shaken with 10% of *d*-limonene still shows the same amount of hydrocarbon in solution, although the solution has become strongly dextrorotatory. The two results are contradictory, but the authors conclude that dipentene is a mixture and not a definite compound.

Experiments have also been made on the solubility of *dl*-ethylpiperidine and mixture of *dl*- with *l*-ethylpiperidine in water at 24·95° and 21·95°. The concentration of the solutions was determined by means of standard hydrochloric acid, using *o*-nitrophenol as

indicator. The results show that the solubility is not affected by the presence of an excess of one of the active constituents. The solution, however, was lævorotatory.

Pure *l*-α-ethylpiperidine is best prepared by resolution of the *dl*-base with Reychler's acid. The *l*-base has D^{23} 0·8451, and $[\alpha]_D$ −21·3°.

Details of the preparation of the *dl*-base are given. J. J. S.

Anomalous Products of Benzoylation. Gustav Heller and Walter Tischner (*Ber.*, 1910, **43**, 2574—2581).—After quoting several instances in which anomalous products are obtained by benzoylation in pyridine or quinoline (Heller and Fiesselmann, Abstr., 1902, i, 779; Heller, Abstr., 1903, i, 827; Scholl and Berblinger, Abstr., 1907, i, 257), the authors describe the following benzoylated substances containing pyridine. By treating a cold pyridine solution of *p*-aminobenzoic acid with benzoyl chloride, the *substance*, $2C_{14}H_{11}O_3N,C_5NH_5$, m. p. above 340°, is obtained, which crystallises in slender needles, forms sparingly soluble *sodium* and *potassium* salts, and retains the pyridine even after steam has been passed through its strongly alkaline solution; the pyridine is removed, however, by hydrochloric acid at 170°, aniline and *p*-aminobenzoic acid being formed. Benzoylation in quinoline or dimethlaniline yields only the normal product. In a similar way, *m*-aminobenzoic acid and *p*-aminophenylacetic acid yield respectively the *substances*, $2C_{14}H_{11}O_3N,C_5NH_5$ and

$$2C_{15}H_{13}O_3N,C_5NH_5$$

(which are precipitated by the addition of dilute hydrochloric acid), together with the normal products of benzoylation. When *p*-benzoylaminobenzoic acid is heated with acetic anhydride, an *isomeride* separates on cooling in tufts of colourless needles; it contains $\frac{1}{4}Ac_2O$, which is removed at 150°, but not by sodium carbonate solution, and has m. p. 240° (softening at 150—155° and resolidifying). The dried substance sinters at 265°, resolidifies, and then slowly decomposes at a much higher temperature; it is not immediately soluble in boiling sodium carbonate, and only dissolves slowly in warm sodium hydroxide, the solution yielding *p*-benzoylaminobenzoic acid by acidification. On account of these properties, the isomeride receives the constitution $C_6H_4<^{NH_2Bz}_{CO-\!-}>O$, and is called p-*benzoylaminobenzoic acid cycloid*. When boiled with acetic anhydride, *p*-acetylaminobenzoic acid yields p-*diacetylaminobenzoic anhydride*, $(NAc_2\cdot C_6H_4\cdot CO)_2O$, m. p. 253—254°.

The paper also contains a reply to the statements of Bamberger (Abstr., 1909, i, 509) and of Mohr (this vol., i, 116) that acetylanthranil contains the 1 : 3-oxazine ring. C. S.

Constitution of Benzoylanthranil. Otto Mumm and Hugo Hesse (*Ber.*, 1910, **43**, 2505—2511).—Two formulæ have been proposed for benzoylanthranil: that of Friedländer and Wleügel (I), and that of Angeli and Angelico (II), of which the latter is considered the

$$C_6H_4<^{N\cdot CO\cdot C_6H_5}_{CO}$$
(I.)

$$C_6H_4<^{N=CPh}_{CO-O}$$
(II.)

more probable. No direct proof of its validity, however, has yet been given, but such is now afforded by the interaction of anthranilic acid with benzanilideiminochloride to form a ring system. From the intermediate product of the reaction, water must be eliminated if the Friedländer-Wleügel formula is correct, and aniline must be eliminated if the Angeli-Angelico formula is the true one. Experiments in absolute ethereal solution, with or without pyridine, proved that aniline is eliminated and benzoylanthranil formed.

Diphenylquinazolone, $C_6H_4<\begin{matrix}N=CPh\\ CO\cdot NPh\end{matrix}$, could not be obtained by the action of benzanilide chloride on anthranil, but it was obtained by shaking sodium anthranilate in aqueous solution with benzanilideiminochloride in ether. It crystallises in prisms, m. p. 158—159°, and has faintly basic properties, the *hydrochloride* having m. p. 172°.

E. F. A.

Preparation of Substituted Indoles by the Catalytic Decomposition of Arylhydrazones. Alexander E. Arbusoff and W. M. Tichwinsky (*Ber.*, 1910, **43**, 2301—2303).—The phenyl- and tolylhydrazones of the lower aliphatic aldehydes and ketones yield substituted indoles when heated with small amounts (0·1 gram) of cuprous chloride at 180—230°. The bases can be isolated by subjecting the crude products to fractional distillation under reduced pressure.

2 : 3-Dimethylindole, 3-methylindole, and 3 : 5-dimethylindole have been prepared from methyl ethyl ketone phenylhydrazone, propaldehydephenylhydrazone, and propaldehyde-*p*-tolylhydrazone respectively.

Zinc chloride and platinous chloride can be used instead of cuprous chloride.

J. J. S.

Syntheses with *o*-Xylylene Bromide. Max Scholtz and R. Wolfrum (*Ber.*, 1910, **43**, 2304—2318. Compare Scholtz, Abstr., 1898, i, 305, 383, 471, 565, 567).—*tert.*-Butylamine reacts with *o*-xylylene bromide in the same manner as other aliphatic primary amines, no steric hindrance is observable, and the product is tert.-*butyldihydro*iso*indole*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot CMe_3$, which crystallises from ethyl alcohol in glistening plates, m. p. 42° and b. p. 125—130°/13 mm. Its *methiodide*, $C_{13}H_{20}NI$, forms colourless crystals, m. p. 221°.

p-Aminoacetophenone (3 mols.) also condenses with *o*-xylylene bromide (1 mol.), yielding p-*acetylphenyldihydro*iso*indole*,

$$C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot C_6H_4\cdot COMe,$$

in the form of glistening plates, m. p. 197°. This compound condenses with aldehydes in the presence of alkalis in much the same manner as *p*-aminoacetophenone itself (Scholtz and Huber, Abstr., 1904, i, 253).

The *benzylidene* derivative, $C_8H_8:N\cdot C_6H_4\cdot CO\cdot CH:CHPh$, crystallises from alcohol in glistening, yellow plates, m. p. 202°; the *cinnamylidene* derivative, $C_8H_8:N\cdot C_6H_4\cdot CO\cdot CH:CH\cdot CH:CHPh$, crystallises from

acetone in slender, orange-coloured needles, m. p. 187°; the *nitrobenzylidene* derivative, $C_{23}H_{18}O_3N_2$, forms a pale yellow, crystalline powder, m. p. 238°. 2-p'-*Dimethylamino*-p-*cinnamoylphenyldihydroisoindole*, $C_8H_8{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2$, crystallises from pyridine in golden-yellow plates, m. p. 196°.

At 100° 2-phenyldihydroisoindole combines readily with methyl iodide, yielding the *methiodide*, $C_8H_8{:}NPh,MeI$, which forms colourless plates, m. p. 177°. 2-Phenyldihydroisoindole condenses readily with aldehydes, especially in the presence of concentrated hydrochloric acid, yielding derivatives of diphenylmethane, or, in the case of aromatic aldehydes, derivatives of triphenylmethane. The condensation takes place in the para-position with respect to the nitrogen atom, as *p*-tolyldihydroisoindole does not react with aldehydes. Formaldehyde reacts without the aid of a condensing reagent, yielding *bisxylyleneaminodiphenylmethane*, $CH_2(C_6H_4{\cdot}N{:}C_8H_8)_2$, which forms slender needles, m. p. 308—309°. *Bisxylyleneaminotriphenylmethane*, $CHPh(C_6H_4{\cdot}N{:}C_8H_8)_2$, separates from a mixture of pyridine and alcohol in colourless, felted needles, m. p. 265°. *Bisxylyleneaminodimethylaminotriphenylmethane*, $NMe_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}N{:}C_8H_8)_2$, crystallises from pyridine in colourless needles, m. p. 185°. *Bisxylyleneaminodiphenylstyrylmethane*, $CHPh{:}CH{\cdot}CH(C_6H_4{\cdot}N{:}C_8H_8)_2$, forms a yellow, crystalline powder, which is not molten at 300°. *Bisxylyleneamino-di*-m-*tolylmethane*, $CH_2(C_6H_3Me{\cdot}N{:}C_8H_8)_2$, obtained from *m*-tolyldihydroisoindole, crystallises from pyridine in colourless needles, m. p. 255°.

Scholtz and Jaross (Abstr., 1901, i, 485) have shown that secondary 1 : 4-diamines condense with alcoholic solutions of aldehydes without the use of a condensing agent; an exception to this rule is xylylene-di-*o*-toluidine, which does not react. It is now shown that this base will condense with aldehydes in the presence of concentrated hydrochloric acid. With formaldehyde, it yields *methylene-di*-o-*tolyl*-o-*xylylenediamine*, $C_6H_4{<}\begin{matrix}CH_2{\cdot}N(C_6H_4Me)\\CH_2{\cdot}N(C_6H_4Me)\end{matrix}{>}CH_2$, as glistening prisms, m. p. 139°, and with benzaldehyde, *benzylidene-di*-o-*tolyl*-o-*xylylenediamine*, $C_6H_4{<}\begin{matrix}CH_2{\cdot}N(C_6H_4Me)\\CH_2{\cdot}N(C_6H_4Me)\end{matrix}{>}CHPh$, m. p. 180°.

Methylamine reacts with xylylenepiperidonium bromide at 200° in much the same manner as ammonia (Abstr., 1898, i, 567), yielding *pentamethylenemethylxylylenediamine*,

$$C_6H_4{<}\begin{matrix}CH_2{\cdot}NMe{\cdot}CH_2{\cdot}CH_2\\CH_2{\cdot}NH{-}CH_2{\cdot}CH_2\end{matrix}{>}CH_2.$$

This is a colourless liquid, b. p. 160—165°/15 mm., and yields a *benzenesulphonyl* derivative, $C_{14}H_{21}N_2{\cdot}SO_2Ph$, m. p. 87°. When distilled, the methyl derivative yields 2-methyldihydroisoindole (Fränkel, Abstr., 1901, i, 45).

The products obtained by the condensation of xylylenepiperidonium bromide with aliphatic secondary amines, and previously represented as $NR_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N{:}C_5H_{10}$, are undoubtedly cyclic compounds of the type $C_6H_4{<}\begin{matrix}CH_2{\cdot}NR{\cdot}CH_2{\cdot}CH_2\\CH_2{\cdot}NR{\cdot}CH_2{\cdot}CH_2\end{matrix}{>}CH_2$. Aromatic primary amines react with xylylenepiperidonium bromide in different ways,

according to the nature of the amine. With aniline at 200°, piperidine and phenyldihydro*iso*indole are formed; *p*-toluidine reacts in a similar manner, but *o*-toluidine does not yield an *iso*indole derivative. The reaction probably consists of a rupture of the original ring, the formation of an eleven-membered ring, and the splitting up of this into the two compounds mentioned.

Dixylyleneammonium bromide (Scholtz, Abstr., 1891, 1353) when heated with piperidine and water at 200° yields a ditertiary base,

$$C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N\cdot CH_2\cdot C_6H_4\cdot CH_2.C_5NH_{10},$$

xylylenepentamethylenexylylenediamine, b. p. 240—245°.

o-Xylylene bromide and tetrahydroquinoline condense in the usual manner, yielding o-*xylylenetetrahydroquinolonium bromide*,

$$C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>NBr{:}C_9H_{10},$$

which is a syrup; the corresponding *iodide*, $C_{17}H_{18}NI$, forms colourless needles, m. p. 238°, and the *picrate*, $C_{17}H_{18}N\cdot O\cdot C_6H_2(NO_2)_3$, yellow needles, m. p. 165°.

Dibenzyl-o-*xylyleneammonium bromide*, $C_8H_8{:}NBr(CH_2Ph)_2$, prepared from *o*-xylylene bromide and dibenzylamine in chloroform solution, crystallises in snow-white plates, m. p. 188°, and when heated with ammonia at 200° yields *dibenzyl*-o-*xylylenediamine*,

$$C_6H_4(CH_2\cdot NH\cdot CH_2Ph)_2,$$

the *hydrochloride* of which has m. p. 251°.

o-*Xylylenediiso**amylammonium bromide* is an oil; the *iodide*, $C_{18}H_{30}NI$, crystallises from water, and has m. p. 139°. The bromide when heated with ammonia at 200° yields o-*xylylenediiso**amyldiamine*, $C_6H_4(CH_2\cdot NH\cdot C_5H_{11})_2$, a colourless oil with b. p. 210°/12 mm.

Dibenzylpiperidonium bromide, $C_5H_{10}{:}NBr(CH_2Ph)_2$, prepared by the action of dibenzylamine on αε-dibromopentane, crystallises in colourless plates, m. p. 253°, and when heated with ammonia at 200° yields benzylamine, dibenzylamine, and benzylpiperidine. o-*Xylylenedipropylammonium bromide*, $C_8H_8{:}NBr(C_3H_7)_2$, crystallises in colourless plates, m. p. 107°, and when heated with ammonia at 200° yields propyl bromide and 2-*propyldihydroisoindole*. The latter is a colourless oil, b. p. 230—240°, and forms a *methiodide*, $C_{11}H_{15}N,MeI$, m. p. 150°. The *platinichloride*, $(C_{11}H_{15}N)_2H_2PtCl_6$, forms a reddish-yellow powder, m. p. 192°. The decomposition of the dipropyl derivative is thus analogous to that of the diethyl salt (Abstr., 1898, i, 568).

2-*Amylenedihydroisoindole*, $C_8NH_8\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$, obtained by treating xylylenepiperidonium bromide with moist silver oxide, evaporating to a syrup, and distilling, has b. p. 140—150°/12 mm. Its *methiodide* is also oily. J. J. S.

New Method for the Synthesis of *iso*Quinoline Bases. Amé Pictet and Alfons Gams (*Ber.*, 1910, **43**, 2384—2391. Compare Abstr., 1909, i, 671).—Acylated carbinols of the type

$$OH\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot R,$$

where R = methyl, phenyl or benzyl, readily undergo condensation when heated with phosphoric oxide and xylene, yielding 1-substituted

*iso*quinolines. Phenylformylaminomethylcarbinol reacts in a similar manner, yielding *iso*quinoline, and this is the most convenient synthetical method for the preparation of the base.

Phenylphenacetylaminomethylcarbinol,

$$OH\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot CH_2Ph,$$

obtained by reducing ω-phenylacetylaminoacetophenone (Robinson, Trans., 1909, 95, 2167) with sodium amalgam, alcohol, and acetic acid, crystallises from water in slender needles, m. p. 123°.

Phenylbenzoylaminomethylcarbinol (Kolshorn, Abstr., 1904, i, 675) is prepared most readily by reducing benzoylaminoacetophenone (Robinson, *loc. cit.*). *Phenylacetylaminomethylcarbinol*,

$$OH\cdot CHPh\cdot CH_2\cdot NHAc,$$

crystallises from benzene in colourless needles, m. p. 104°. 1-Benzyl-*iso*quinoline forms colourless needles, m. p. 56°. 1-*Phenyl*isoquinoline, $C_{15}H_{11}N$, crystallises from dilute alcohol in colourless needles, m. p. 93°, b. p. 298°/729 mm. The *hydrochloride* has m. p. 235—236°; the *picrate*, m. p. 164·5°, and the *platinichloride* forms red needles, m. p. 242° (decomp.).

1-*Methyl*isoquinoline, $C_{10}H_9N$, is a colourless oil, b. p. 243—245°/728 mm. The *hydrochloride* forms colourless needles, m. p. about 170°; the *sulphate* forms colourless prisms, m. p. 245°; the *picrate* has m. p. 206—208°; the *dichromate* forms red prisms, sparingly soluble in water, and decomposes at about 150°; the *platinichloride*,

$$2C_{10}H_9N,H_2PtCl_6,2H_2O,$$

forms reddish-yellow prisms, and melts at 201·5° when anhydrous. The base is probably identical with the two methyl*iso*quinolines described in Beilstein.

ω-*Formylaminoacetophenone*, $COPh\cdot CH_2\cdot NH\cdot CHO$, prepared by the action of crystallised formic acid on ω-aminoacetophenone hydrochloride, crystallises from a mixture of benzene and light petroleum in large, flat prisms, m. p. 70—71°, and when reduced with sodium amalgam, alcohol, and formic acid yields *phenylformylaminomethylcarbinol*, $OH\cdot CHPh\cdot CH_2\cdot NH\cdot CHO$, as a reddish-brown, crystalline mass. J. J. S.

Preparation of a Dihydroxycarbazoledisulphonic Acid. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 224952).—The product obtained by fusing carbazoledisulphonic acid with an alkali hydroxide has been described (Schultz and Hauenstein, Abstr., 1907, i, 1074), but whether the product was a dihydroxy- or a hydroxycarbazolesulphonic acid is not definitely stated.

When carbazole is treated with fuming sulphuric acid (five parts) at a temperature not exceeding 40°, and then slowly heated to 100°, disulphonation takes place; if this mixture is further treated with two parts of sulphuric acid (containing 65% SO_3) and kept at 90—100° until the product ceases to be separable on the addition of salt, *carbazoletetrasulphonic acid* is obtained, and finally isolated by evaporation in the form of its *potassium* salt.

Dihydroxycarbazoledisulphonic acid is prepared from the foregoing acid by fusion with alkali hydroxide at a temperature of 240—300°;

the *potassium* salt forms colourless needles containing $4H_2O$, and shows a green fluorescence on addition of ammonium hydroxide.

The free acid can be isolated from its *barium* salt.

F. M. G. M.

[Preparation of *N*-Alkyl- and of *N*-Aryl-carbazoles and their Indophenol Derivatives.] Leopold Cassella & Co. (D.R.-P. 224951).—The *N*-alkyl-carbazoles have been previously described; it is now found that *N*-aryl-carbazoles can be prepared in analogous manner, and that they likewise, when heated with polysulphides, yield valuable dyes.

9-*Benzylcarbazole*, colourless needles, m. p. 118—120°, is prepared by the action of benzyl chloride on potassium carbazole at high temperatures or under pressure.

9-*Phenylcarbazole* is obtained by heating potassium carbazole with bromobenzene in the presence of copper powder under pressure at a temperature of 180—220°; it forms colourless needles, m. p. 82—84°.

9-p-*Tolylsulphonylcarbazole*, pale yellow needles, m. p. 127—128°, is prepared from potassium carbazole and *p*-toluenesulphonyl chloride. These substances combine with *p*-nitrosophenol, yielding dark blue powders, which on reduction form greyish-white, crystalline leuco-compounds.

F. M. G. M.

Condensation Products from Salicylidene- and Hydrocyano-salicylidene-aniline (Anilino-*o*-hydroxyphenylacetonitrile). Georg Rohde and G. Schärtel (*Ber.*, 1910, **43**, 2274—2286).—Miller and Plöchl (*Ber.*, 1896, **27**, 1730; 1898, **29**, 2699) have shown that Schiff's bases do not undergo the benzoin condensation with potassium cyanide. The product obtained by Schwab (Abstr., 1901, i, 380) by condensing *o*-hydroxybenzylideneaniline with an alcoholic solution of potassium cyanide is shown to be 4-cyano-3-phenyl-2-*o*-hydroxyphenyl-3 : 4-dihydro-1 : 3-benzoxazine, $C_6H_4<\begin{matrix}O\text{———}CH\cdot C_6H_4\cdot OH\\ CH(CN)\cdot NPh\end{matrix}$, and not to have the constitution ascribed to it by Schwab. The product is prepared most readily by shaking vigorously for three hours an alcoholic solution of aniline (1 mol.) and salicylaldehyde (2 mols.) with an alcoholic solution of potassium cyanide (1 mol.). When its ethereal solution is hydrolysed with concentrated hydrochloric acid, the products are salicylaldehyde and the acid amide hydrocyanosalicylideneaniline, *anilino-o-hydroxyphenylacetamide*, $OH\cdot C_6H_4\cdot CH(NHPh)\cdot CO\cdot NH_2$, which yields a *hydrochloride*, $C_{14}H_{14}O_2N_2,HCl$, crystallising from alcohol in colourless needles, m. p. 183°. The amide crystallises from benzene in colourless needles containing benzene and melting at 63°; when further heated, it gives up benzene, solidifies, and then has m. p. 126° The same amide can be prepared by adding Miller and Plöchl's hydrocyanosalicylideneaniline (anilino-*o*-hydroxyphenylacetonitrile) to concentrated hydrochloric acid.

Schwab's condensation product can be synthesised by shaking an alcoholic solution of hydrocyanosalicylideneaniline with salicylaldehyde and potassium hydroxide dissolved in a little water. The following derivatives are described: *Sodium* salt, $C_{21}H_{15}O_2N_2Na$, yellow,

glistening powder, m. p. 249°, obtained by shaking an ethereal solution of the 1 : 3-benzoxazine with 10% sodium hydroxide solution; *benzoyl* derivative, $C_{28}H_{20}O_3N_2$, yellow crystals, m. p. 188°; *benzenesulphonyl* derivative, $C_{27}H_{20}O_4N_2S$, glistening needles from alcohol, m. p. 162°.

Hydrocyanosalicylideneaniline and benzaldehyde undergo condensation in the presence of potassium hydroxide, yielding 4-*cyano* 2 : 3-*diphenyl*-2 : 4-*dihydro*-1 : 3-*benzoxazine*, $C_6H_4<\begin{matrix}O\text{———}CHPh\\ CH(CN)\cdot NPh\end{matrix}$, in the form of yellow needles, m. p. 138°.

When molecular quantities of salicylideneaniline and potassium cyanide are condensed, a *product*, $C_{14}H_{12}ON_2$, is formed, which crystallises from benzene in compact prisms, m. p. 135—137°. The same product is formed by condensing salicylaldehyde and salicylideneaniline with potassium cyanide or salicylidene-aniline and hydrocyanosalicylideneaniline with potassium cyanide. It is isomeric with hydrocyanosalicylideneaniline, from which it can be obtained by shaking with potassium cyanide, potassium carbonate, or sodium ethoxide solutions.

A by-product formed in the preparation of the benzoxazine separates as dark red needles from the mother liquors after a time, and can be obtained most readily by boiling an alcoholic solution of aniline, salicylaldehyde, and potassium cyanide for two to three hours. It can be crystallised from pyridine, has m. p. 258°, and is stable towards acids. Its *acetyl* derivative crystallises from alcohol in pale yellow needles, m. p. 195°, and its *benzoyl* derivative in yellowish-brown prisms, m. p. 227°. J. J. S.

Catalytic Decomposition of Phenylhydrazine by means of Cuprous Halides. Alexander E. Arbusoff and W. M. Tichwinsky (*Ber.*, 1910, **43**, 2295—2296. Compare Struthers, Proc., 1905, **21**, 95).—At 150° phenylhydrazine reacts with cuprous halides according to the equation: $3NHPh\cdot NH_2 + CuCl = 3NH_2Ph + N_2 + NH_3 + CuCl$. The reaction is preceded by the formation of an additive compound, for example, the *compound*, $2NHPh\cdot NH_2,CuI$, has been isolated as colourless prisms, which begin to decompose at 150°.

The rate of decomposition with the different halides has been determined; the reaction proceeds most rapidly with the chloride, and least readily with the iodide. If sufficient care is not taken, the reaction with cuprous chloride may become explosive. J. J. S.

Nitrosophenylhydrazine. Eugen Bamberger and H. Hauser (*Annalen*, 1910, **375**, 316—333).—The preparation and properties of nitrosophenylhydrazine are described, and also many of its reactions, chiefly in the form of test-tube experiments. It acts as a pronounced reducing agent towards mercuric nitrate, yellow mercuric oxide, silver nitrate, and calcium hypochlorite, being itself oxidised mainly to nitrosobenzene (detected by its odour). Its alcoholic solution, as concentrated as possible, yields at $-12°$ to $-15°$ with a cold saturated alcoholic solution of cupric acetate, *copper nitrosophenylhydrazine*, $Cu(C_6H_6ON_2)_2$, which forms copper-red leaflets with a bronze lustre, is extremely explosive, and inflames in contact with concentrated sulphuric or nitric acid. The solution of the metallic derivative in

acetone gives, almost immediately, a precipitate of copper sulphide with hydrogen sulphide; the reaction, however, is not regarded as ionic, the substance being probably an internally complex salt. When the red copper derivative is treated with acetic acid containing a little water (the absence of water prevents the reaction), nitrogen is evolved and pale grey needles of copper nitrosophenylhydroxylamine are produced. This copper derivative is more conveniently obtained by treating an alcoholic solution of nitrosophenylhydrazine at 0° with a solution (saturated at 5°) of copper acetate in glacial acetic acid (the reaction fails in the presence of 13—15% of water), or by adding nitrosophenylhydrazine to ammoniacal copper hydroxide at −16°. This indirect conversion of nitrosophenylhydrazine into nitrosophenylhydroxylamine is not a case of simple hydrolysis: $NH_2{\cdot}NPh{\cdot}NO + H_2O = OH{\cdot}NPh{\cdot}NO + NH_3$, since it is not appreciably brought about by alkaline reagents, but is probably due to oxidation by the copper oxide: $NH_2{\cdot}NPh{\cdot}NO + O \longrightarrow OH{\cdot}NPh{\cdot}NO + N_2$.

The paper closes with some adverse criticisms of the symmetrical formula, NHPh·NH·NO, suggested by Thiele for nitrosophenyl hydrazine in consequence of its decomposition into aniline and nitrous oxide; in the authors' opinion nitrosophenylhydrazine, like nitrosophenylhydroxylamine (Abstr., 1909, i, 977), is tautomeric:

$$NH_2{\cdot}NPh{\cdot}NO \rightleftarrows NH{:}NPh{:}N{\cdot}OH \left(\text{or } NH{<}\begin{matrix}NPh\\ |\\ N{\cdot}OH\end{matrix}\right),$$

its compounds with heavy metals being derived from either of the latter formulæ. C. S.

Constitution of Nitrosophenylhydrazine. Johannes Thiele and Karl Sieglitz (*Annalen*, 1910, **375**, 334—335).—The suggestion advanced by Thiele (Abstr., 1908, i, 927), that nitrosophenylhydrazine has the constitution NHPh·NH·NO has been withdrawn, because benzoylnitrosophenylhydrazine, obtained by the benzoylation of nitrosophenylhydrazine, is converted by stannous chloride and hydrochloric acid into *s*-benzoylphenylhydrazine, from which the benzoylnitrosophenylhydrazine is regenerated by sodium nitrite and acetic acid. C. S.

α-Acylated Phenylhydrazines. Oskar Widmann (*Ber.*, 1910, **43**, 2595).—The author's method of preparing α-acylated phenylhydrazines (Abstr., 1893, i, 411; 1894, i, 57, 512; 1895, i, 31) has been overlooked by Lockemann (this vol., i, 636). C. S.

Influence of the Halogens on Phototropy in Hydrazones. F. Graziani (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 190—193. Compare this vol., i, 509).—Some hydrazones derived from *p*-bromophenylhydrazine have been prepared to ascertain if the lack of phototropy in certain chloroaniline derivatives (compare Senier and Shepheard, Trans., 1909, **95**, 1943) is due to the presence of the halogen. Of the eight hydrazones examined, four are more or less phototropic, but much less so than the *p*-tolylhydrazones.

Benzaldehyde-*p*-bromophenylhydrazone has m. p. 129° (Biltz and Sieden, Abstr., 1903, i, 120, gave 127·5°), and is phototropic.

Anisaldehyde-*p*-bromophenylhydrazone, m. p. 150° (Ott, Abstr., 1905, i, 376, gave 146—147°), is not phototropic.

Cinnamaldehyde-p-*bromophenylhydrazone*, $C_6H_4Br\cdot N_2H{:}CH\cdot CH{:}CHPh$, crystallises in greenish-yellow, lustrous needles, m. p. 143°, and is phototropic.

Cuminaldehyde-p-*bromophenylhydrazone*, $C_6H_4Br\cdot N_2H{:}CH\cdot C_6H_4\cdot CHMe_2$, forms yellow, phototropic needles, m. p. 135°.

Piperonaldehyde-p-*bromophenylhydrazone*, $C_6H_4Br\cdot N_2H{:}CH\cdot C_6H_3{:}O_2{:}CH_2$, crystallises in colourless laminæ, m. p. 155° (decomp.), and is not phototropic.

p-*Tolualdehyde*-p-*bromophenylhydrazone*, $C_6H_4Br\cdot N_2H{:}CH\cdot C_6H_4Me$, forms small, yellow laminæ, m. p. 162° (decomp.), and is not phototropic.

Vanillin-*p*-bromophenylhydrazone is non-phototropic.

Salicylaldehyde-*p* bromophenylhydrazone has m. p. 171—172° (Biltz and Sieden, *loc. cit.*, gave 175·5°), and is slightly phototropic.

R. V. S.

Relations between Constitution and Phototropy. Maurice Padoa and F. Graziani (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 193—196. Compare this vol., i, 509, and preceding abstract).—The authors have obtained a number of hydrazones derived from 1 : 4 : 5- and 1 : 3 : 5-xylylhydrazines, and have prepared the latter substance for the first time. In agreement with the regularity previously observed, the 1 : 4 : 5-derivatives do not exhibit phototropy. Of the four 1 : 3 : 5-compounds, one is very feebly phototropic.

1 : 4 : 5-Xylylhydrazine hydrochloride has m. p. 209°; Plancher and Caravaggi (Abstr., 1905, i, 158) gave 206°.

Benzaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CHPh$, forms small, yellow needles, m. p. 89°.

Anisaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4\cdot OMe$, crystallises in small, yellowish-white laminæ, m. p. 117°.

Cinnamaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot CH{:}CHPh$, forms small, yellow needles, m. p. 121°.

Cuminaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4\cdot CHMe_2$, crystallises similarly, and has m. p. 85°.

Piperonaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_3{:}O{:}CH_2$, crystallises in yellow scales, m. p. 135°.

p-*Tolualdehyde*-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4Me$, forms minute, pale yellow scales, m. p. 109°.

Vanillin-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_3(OH)\cdot OMe$, crystallises in very small, colourless needles, m. p. 158°.

Salicylaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H{:}CH\cdot C_6H_4\cdot OH$, forms pale yellow scales, m. p. 134°.

1 : 3 : 5-*Xylylhydrazine hydrochloride* was prepared by diazotisation

of the corresponding xylidine. It is very soluble in concentrated hydrochloric acid, and was not obtained in pure condition.

Cinnamaldehyde-1 : 3 : 5-*xylylhydrazone* forms yellow crystals, m. p. 142—143° (becoming slightly brown), and is phototropic.

p-*Tolualdehyde*-1 : 3 : 5-*xylylhydrazone* crystallises in rosettes of yellow needles, m. p. 119°, and is not phototropic.

Piperonaldehyde-1 : 3 : 5-*xylylhydrazone* forms yellow, non-phototropic needles, m. p. 135—136° (yielding a brown liquid).

Anisaldehyde-1 : 3 : 5-*xylylhydrazone* crystallises in small, yellow needles, m. p. 144—145° (giving a brown liquid). R. V. S.

Preparation and Phototropy of Some Osazones. Maurice Padoa and L. Santi (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 302—307. Compare Padoa and Graziani, this vol., i, 509).—Continuing the study of phototropy, the authors have prepared osazones from benzil and piperil with *o*- and *p*-tolyl- and *β*-naphthyl-hydrazines. Even on combining these results with those of Biltz (Abstr., 1900, ii, 125), no connexion between constitution and phototropy becomes evident. Of the two isomeric forms to be expected, only the *β*-modification was obtained in every case.

β-Benzil-p-*tolylosazone*. $C_2Ph_2(:N\cdot NH\cdot C_6H_4Me)_2$, obtained by Pickel's method (Abstr., 1886, 545), is a yellow, crystalline, phototropic substance, m. p. 152°.

β-Piperil-p-*tolylosazone*, $\begin{matrix}CH_2{:}O_2{:}C_6H_3\cdot C{:}N\cdot NH\cdot C_6H_4Me\\ CH_2{:}O_2{:}C_6H_3\cdot C{:}N\cdot NH\cdot C_6H_4Me\end{matrix}$, similarly prepared, crystallises in small, sulphur-yellow needles, m. p. 215°, and is phototropic.

β-Benzil-β-naphthylosazone, $C_2Ph_2(:N\cdot NH\cdot C_{10}H_7)_2$, obtained by the same method, forms yellow needles, m. p. 211·5°. It is phototropic, and one specimen of it showed phototropic change in either direction with remarkable rapidity, possibly owing to the presence of some impurity catalytically affecting the process.

β-Piperil-β-naphthylosazone, similarly prepared, is a yellow, crystalline, phototropic substance, m. p. 207°.

β-Benzil-o-*tolylosazone* was prepared by Purgotti's method (*Gazzetta*, 1892, **14**, ii, 611), and forms a canary-yellow, crystalline, phototropic powder, m. p. 170°.

β-Piperil-o-*tolylosazone*, obtained by the same method, is a yellow, crystalline powder, m. p. 206·5°, and is phototropic. It becomes bright red instantly in sunlight, and may be said to be the most sensitive phototropic substance yet prepared. R. V. S.

Rearrangement in the Quinone Group. Ernst Börnstein (*Ber.*, 1910, **43**, 2380—2384).—The base obtained by the action of sulphuric acid on *p*-toluidino-*p*-toluquinonetolylimide (Abstr., 1901, i, 376) has the same composition as the original compound, and is regarded as 7-p-*toluidino*-3 : 6-*dimethylphenoxazine*,

$$C_7H_7\cdot NH\cdot C_6H_2Me\begin{matrix}O\\ NH\end{matrix}C_6H_3Me.$$

It crystallises from ethyl alcohol or dilute acetone in brownish, orange-yellow needles or plates, m. p. 173°. The *hydrochloride*, $C_{21}H_{20}ON_2,HCl$,

forms red rhombohedra, with a greenish, metallic reflex. The *platinichloride*, $2C_{21}H_{20}ON_2,H_2PtCl_6$, has a yellowish-red colour. The *sulphate*, $C_{21}H_{20}ON_2,H_2SO_4$, crystallises from alcohol in deep, red compact cubes. The *picrate*, $C_{27}H_{23}O_8N_5$, forms golden-yellow, microscopic needles, m. p. 227°. The base yields a phenylcarbimide *derivative*,

$$C_{21}H_{20}ON_2,C_7H_5ON,$$

as colourless rosettes of needles, m. p. 188° (decomp.).

Attempts to acetylate, methylate, and form an oxime gave negative results. When reduced, the base yields *p*-toluidine. J. J. S.

Preparation of 5 : 5-Dialkylbarbituric Acids. Alfred Einhorn (D.R.-P. 225457).—The action of oxalyl chloride on dialkylmalonamides affords 78—80% of the theoretical yield of the respective dialkylbarbituric acid.

Equal weights are heated together on the water-bath during several hours, water is added, and the product collected. F. M. G. M.

Condensation Products of Alloxan. Otto Kühling (*Ber.*, 1910, **43**, 2406—2417. Compare Abstr., 1905, i, 944; 1908, i, 571; Kühling and Schneider, *ibid.*, 1909, i, 424).—Alloxan condenses with ethyl benzoylacetate or the corresponding methyl ester in the presence of a mixture of water and alcohol, saturated at −6° to −8°, with hydrogen chloride, yielding carbethoxy- or carbomethoxy-phenacyldialuric acid. These compounds resemble the phenacyldialuric acids as regards their behaviour towards dilute acids or acetic anhydride, but are readily decomposed into their components when boiled with water, mixed with sodium carbonate solution at the ordinary temperature, or treated with the usual reagents for ketones. The acetyl derivatives, are more stable, and react with sodium carbonate solution, yielding compounds which are regarded as carbethoxy(methoxy)-phenacylbarbituric acids.

Carbethoxyphenacyldialuric acid,

$$CO_2Et\cdot CHBz\cdot C(OH)<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

crystallises from alcohol in rhombic prisms, m. p. 207—208° (decomp.) after turning red at 180°. When boiled for several hours with 12% hydrochloric acid, it yields phenacyldialuric acid. The *acetyl* derivative, $CO_2Et\cdot CHBz\cdot C(OAc)<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO$, crystallises in long plates, melts at 167—168°, then solidifies, and melts again at 235—236°. *Carbethoxyphenacylbarbituric acid*, $CO_2Et\cdot CHBz\cdot CH<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO$, crystallises from alcohol in prisms, m. p. 239—240°, and is also formed when the acetyl derivative is heated at 180—190°. It yields a *sodium* salt, $C_{15}H_{13}O_6N_2Na$, in the form of prismatic needles, and reacts with benzenediazonium chloride solution, yielding alloxanphenylhydrazone. With phenylhydrazine in acetic acid solution, the barbituric acid yields a yellow, amorphous precipitate, and yellowish-red crystals of a *compound*, $C_{21}H_{18}ON_4$, m. p. 174—175°, which is probably a *keto-anilinodiphenyltetrahydrotriazine*, $CPh<\begin{matrix}CH_2\text{——}CO\\|\\N\cdot NPh\cdot N\cdot NHPh\end{matrix}$.

Carbomethoxyphenacyldialuric acid,

$$CO_2Me\cdot CHBz\cdot C(OH)<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

forms colourless prisms, m. p. 221° (decomp.). The *acetyl* derivative, $C_{16}H_{14}O_8N_2$, also forms prisms, melts at 158°, resolidifies, and again melts at 241—242°. *Carbomethoxyphenacylbarbituric acid*, $C_{14}H_{12}O_6N_2$, forms colourless needles, m. p. 246—247° (decomp.). J. J. S.

Compounds of Piperazine with Phenols. H. Stévignon (*Bull. Soc. chim.*, 1910, [iv], 7, 922—926).—Schmidt and Wichmann have shown that piperazine forms additive compounds with phenol and with quinol (Abstr., 1892, 210), and the author has extended this observation to other phenols, and finds that 1 mol. of piperazine combines with 2 mols. of a monohydric phenol or with 1 mol. of a dihydric phenol. In all cases the two substances were allowed to react in alcohol.

The following substances were prepared: *Di-o-cresolpiperazine*, m. p. 51—52° (approx.), pale yellow crystals. *Dicarvacrolpiperazine*, m. p. 85—86° (approx.), colourless needles. *Dithymolpiperazine*, m. p. 88°, brilliant, colourless needles. *Di-β-naphtholpiperazine*, m. p. 110° (approx.), greyish-white crystals. *Catecholpiperazine*, bright brown needles. *Diguaiacolpiperazine*, m. p. 98° (approx.), brilliant colourless lamellæ. The piperazine in these compounds behaves as a diacidic base, and can be titrated directly with *N*/10-sulphuric acid, using helianthin-*A* as indicator. T. A. H.

Action of Sulphuric and Hydrochloric Acids on *endo*Bisazo-derivatives. I. Henri Duval (*Bull. Soc. chim.*, 1910, [iv], 7, 915—922).—It is shown that under the action of sulphuric or hydrochloric acid, the *endo*bisazo-compounds behave like azodiazo-compounds, one azo-group being replaced by a hydroxyl group, which in the case of hydrochloric acid is then replaced by chlorine, whilst the second remains intact. Instances of this reaction have been given already (Abstr., 1907, i, 663), and are now repeated with experimental details. The author suggests that the substances now called indazoles should be re-named *iso*azindoles, and that the present *iso*azindoles should be named azindoles.

When 4 : 4′-diacetylbisazodiphenylmethane [4 : 6′-diacetylphenylbenz*iso*indazole] (Abstr., 1908, i, 706) is heated with a 53% solution of sulphuric acid at 100—105°, it is converted in the course of a few minutes into 2′-hydroxy-4 : 6′-diacetyl-3-phenylbenz*iso*indazole,

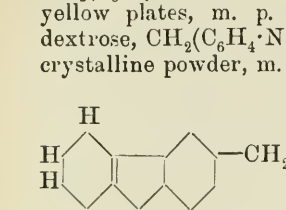
$$HO\cdot C_6H_3Ac\cdot CH<\begin{matrix}-\!\!-\!\!-\!\!-N\\C_6H_3Ac\end{matrix}>N,$$

which in the author's new nomenclature would be "2′-hydroxy-4′ : 6-diacetyl-3-phenylindazole." It melts at 235°, forms bright yellow needles from alcohol, and is soluble in dilute sodium hydroxide solution, but not in ammonia. T. A. H.

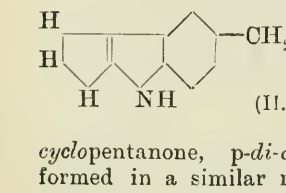
Quinoline and Indole Derivatives from *para*Diaminodiphenylmethane. Walther Borsche and G. A. Kienitz (*Ber.*, 1910, **43**, 2333—2337).—6 : 6′-*Diquinolylmethane*, $CH_2(C_9NH_6)_2$, can be prepared from *p*-diaminodiphenylmethane by the usual Skraup synthesis. It

forms a limpid, brown oil, which solidifies slowly, and can be obtained as colourless needles, m. p. 160°.

4:4′-*Dihydrazinodiphenylmethane*, $CH_2(C_6H_4\cdot NH\cdot NH_2)_2$, prepared by diazotising β-diaminodiphenylmethane and reducing the diazo-compound by Fischer's method, crystallises from benzene in colourless plates, m. p. 71—72°, but turns brown in the course of a few hours when exposed to the air. The *hydrochloride* forms a white, crystalline powder, and is somewhat more stable. The *dibenzylidene* derivative, $CH_2(C_6H_4\cdot NH\cdot N{:}CHPh)_2$, crystallises from glacial acetic acid in golden-yellow plates, m. p. 193—194°. The condensation product with dextrose, $CH_2(C_6H_4\cdot NH\cdot N{:}CH\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH)_2$, is a dark yellow, crystalline powder, m. p. 122—123° (decomp.).



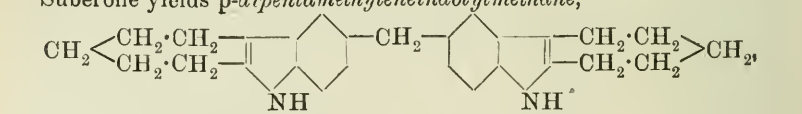
(I.)



(II.)

The condensation product with *cyclo*hexanone readily loses ammonia when warmed with glacial acetic acid (Abstr., 1908, i, 365), and yields p-*di-aβ - tetramethyleneindolyl methane* (*bistetrahydrocarbazolylmethane*, formula I.), which separates from dilute acetone in yellow crystals, m. p. 265°. From *cyclo*pentanone, p-*di-aβ-trimethyleneindolylmethane* (formula II) is formed in a similar manner; it separates from dilute acetic acid in a yellow powder, m. p. 262°.

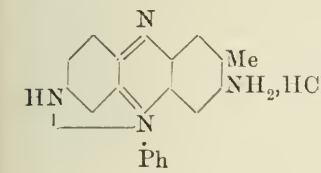
Suberone yields p-*dipentamethyleneindolylmethane*,



which does not melt at 300°. J. J. S.

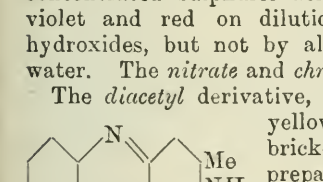
Synthesis of the Safranines. W. G. Saposhnikoff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 505—512. Compare Barbier and Sisley, Abstr., 1905, i, 840).—The author disagrees with the ordinarily accepted view of the formation of the safranines and indulines, namely, that the first products of the reaction are indamines which then condense with the amines. *p*-Benzoquinonedi-imide is quite inert towards amines, only reacting when one of the hydrogen atoms of the amino-group is displaced by a halogen, and this the more readily the greater the atomic weight of the halogen. It is, therefore, probable that the first product in the formation of the safranines is *p*-benzoquinonedichlorodi-imide (or a similar compound), which then reacts with the amines. The tertiary amines only form these condensation products when they have the property of readily losing one of their radicles. The secondary and primary amines are equally active, although some primary amines, such as tribromoaniline and dibromotoluidine, do not react at all or with difficulty. In all cases an excess of the amine is favourable to a good yield, and as the molecular weight of the amine increases, the number of molecules

of the amine that combine with one of the *p*-benzoquinonedichlorodi-imide decreses. Polyamines, particularly *m*-diamines, react readily with *p*-benzoquinonedichlorodi-imide. If in a mixed secondary and primary amine, a methyl group is introduced in an ortho-position to the primary amino-group, the compound so formed reacts very readily with *p*-benzoquinonedichlorodi-imide. Thus 4-phenyltolylene-2 : 4-diamine reacts readily with the quinone, forming the leuco-compound of indamine, which passes readily into indamine and then by loss of the heavier amino-group can be converted into the azone (annexed formula), which is the formula proposed for safranine. Its advantages over the formula hitherto accepted are discussed. Thus it readily explains why only one amino-group reacts when safranine is diazotised ; also, why only a monoacetyl derivative is obtained and so forth. This method of obtaining safranines is claimed to be far better than any method hitherto described. Z. K.



Synthesis of the Simplest Safranine: 3 : 6-Diamino 5-phenazonium Chloride. W. G. Saposhnikoff and N. N. Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 512—522. Compare preceding abstract).—3 : 6-*Diamino-5-phenyl-2-methylphenazonium chloride* was prepared by heating a mixture of *p*-benzoquinonedichlorodi-imide (1 mol.) and 4-phenyltolylene-2 : 4-diamine (2 mols.) in alcoholic solution on a water-bath for fifteen to twenty minutes. The yield is 86·7—93·2% of the theoretical. The substance forms bright yellow crystals soluble in concentrated sulphuric acid with an emerald-green colour, turning violet and red on dilution. The base is precipitated by alkali hydroxides, but not by alkali carbonates, and is readily soluble in water. The *nitrate* and *chromate*, $(C_{19}H_{17}N_4)_2Cr_2O_7$, were prepared.

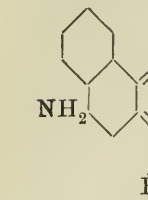
The *diacetyl* derivative, $C_{23}H_{21}O_2N_4Cl$, crystallises from alcohol in yellowish-green, and from glacial acetic acid in brick-red, crystals, of which the chromate was prepared. By eliminating one amino-group by means of the diazo-reaction, monomethyl*apo*safranine (annexed formula) is obtained (compare Kehrmann and Wetter, Abstr., 1898, i, 437). It forms a *chromate*, $(C_{19}H_{16}N_3)_2Cr_2O_7$.



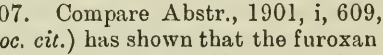
By removing the amino-group from methyl*apo*safranine, or both amino-groups from the original safranine, phenotoluophenazonium is formed. Diazosafranine condenses with β-naphthol to form a blue *dye*, of which the *chromate*, $(C_{29}H_{22}O_2N_5)_2Cr_2O_7$, was analysed. Z. K.

Synthesis of Safranine with a Naphthalene Nucleus (3 : 6-Diamino-5-phenyl-2-methylnaphthaphenazonium Chloride). N. N. Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 522—530. Compare preceding abstract).—3 : 6-*Diamino-5-phenyl-2-methylnaphthaphenazonium chloride*, prepared from naphthaquinonedichlorodi-imide and 4-phenyltolylene-2 : 4-diamine, forms yellowish-green crystals; the *chromate*, $(C_{23}H_{19}N_4)_2Cr_2O_7$, is described. By eliminating one amino-

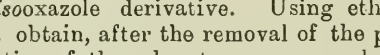
group, the *monoamino*-compound (annexed formula) is obtained, of which the *chromate*, $(C_{23}H_{18}N_3)_2Cr_2O_7$, was analysed; the *acetyl* derivative forms green crystals. On removing the amino-group, the chromogen, 5-*phenyl*-2-*methylnaphthaphenazonium*, isolated as the *ferrichloride*, $C_{23}H_{17}N_2Cl_4Fe$, m. p. 205°, is obtained. The latter is converted, in ammoniacal solution, into the amino-compound. The diazotised naphthasafranine gives a blue *dye* with β-naphthol, the *chromate*, $(C_{33}H_{24}ON_5)_2Cr_2O_7$, of which was analysed. Z. K.

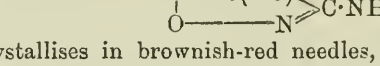


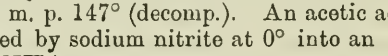
Furoxans. IV. Action of Amines on Dibenzoylfuroxan. Heinrich Wieland and Erwin Gmelin (*Annalen*, 1910, 375, 297—307. Compare Abstr., 1901, i, 609, 610).—The authors' recent work (*loc. cit.*) has shown that the furoxan ring is very easily ruptured by ammonia or amines, amidoximes being produced, thus:



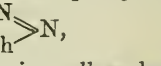
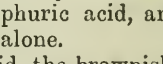
Under suitable conditions the amidoxime may experience ring closure, with the production of *iso*oxazole derivatives. These results are utilised to show that Boeseken's benzoyl-*p*-bromoanilinofurazan (this vol., i, 643), obtained by warming diphenyldinitrosacyl (dibenzoylfuroxan) with ethereal *p*-bromoaniline, is not a furazan, but a nitroso*iso*oxazole derivative. Using ethereal aniline (2 mols.), the authors obtain, after the removal of the precipitated benzanilide and evaporation of the solvent, an orange-coloured syrup of the unstable anilino-oxime, OH·N:CBz·C(:N·OH)·NHPh, which is converted by warm acetic acid into 4-*nitroso*-3-*anilino*-5-*phenyl*isoo*xazole*,



this crystallises in brownish-red needles, and is reduced in alcoholic solution by zinc dust and acetic acid to 4-*amino*-3-*anilino*-5-*phenyl*iso*oxazole*, m. p. 147° (decomp.). An acetic acid solution of the latter is converted by sodium nitrite at 0° into an unstable, red nitrosoamine,  , which rapidly changes to *diphenyl*-3 : 4-gem-*triazolo*isoo*xazole* (3 : 4-*phenylazimino*-5-*phenyl*isoo*xazole*),



m. p. 151° (decomp.), which crystallises in yellow leaflets, gives a magenta coloration with phenol and sulphuric acid, and develops a dark green coloration with sulphuric acid alone.

When warmed with alcohol or acetic acid, the brownish-red nitroso-anilinophenyl*iso*oxazole is converted into the isomeric, colourless azoxime, 3-benzoyl-5-anilino-1 : 2 : 4-oxadiazole,  (as stated by Böeseken), the formation of which is explained by the intermediate production of the furazan ring,  ,

which then undergoes a partial Beckmann transformation (Böeseken, *loc. cit*).

[With Alex. Roseeu.]—Results similar to the preceding are obtained when dibenzoylfuroxan is decomposed by *p*-anisidine. 4-*Nitroso*-3-p-*anisidino*-5-*phenyl*isooxazole, decomp. 123°, crystallises in glistening, black needles, forms dark red solutions, is converted by boiling alcohol mainly into the isomeric azoxime, and is reduced by zinc and acetic acid to 4-*amino*-3-p-*anisidino*-5-*phenyl*isooxazole, m. p. 151°. This base in acetic acid is converted by sodium nitrite into *phenyl*-p-*anisyl*-3 : 4-gem-*triazolo*isooxazole,

$$O<\begin{matrix}CPh:C\text{——————}N\\ \|\quad\quad\quad\quad\quad\quad|\\ N{=}{=}C\cdot N(C_6H_4\cdot OMe)\end{matrix}>N,$$

decomp. 141°, which crystallises in golden-yellow leaflets.

Contrary to Böeseken's statement that dibenzoylfuroxan only reacts with primary amines, the authors find that a vigorous reaction occurs with ethereal piperidine. C. S.

Urazoles. XVII. Rearrangement of the Tautomeric Salts of 1 : 4-Diphenyl-5-thionurazole and 1 : 4-Diphenyl-5-thiolurazole. Sidney Nirdlinger and Salomon F. Acree (*Amer. Chem. J.*, 1910, 44, 219—251).—The slow rearrangement of tautomeric acids and their final states of equilibrium have been investigated by several authors, but the tautomeric salts of such acids have not hitherto been studied. In view of the importance of such work as a test of the validity of Acree's theory, an investigation has now been made of the salts of 1 : 4-diphenyl-5-thionurazole and 1 : 4-diphenyl-5-thiolurazole.

It has been shown by Busch and Holzmann (Abstr., 1901, i, 234) that Marckwald's thiosemicarbazides (Abstr., 1893, i, 46) are structural isomerides of the types $NH_2\cdot NR\cdot CS\cdot NHR$ and

$$NHR\cdot NH\cdot CS\cdot NHR.$$

By the action of carbonyl chloride on $\beta\delta$ diphenylthiosemicarbazide, a compound, m. p. 141°, is obtained, which was regarded by Busch and Holzmann (*loc. cit.*) as 5-thiol-1 : 4-diphenylurazole,

$$NPh<\begin{matrix}C(SH)\cdot NPh\\ >O\quad|\\ C\text{——}N\end{matrix}.$$

Busch (Abstr., 1902, i, 322) has stated that when this substance is heated, it undergoes transformation into a compound, m. p. 219—221°, which he assumed to be 5-thion-1 : 4-diphenylurazole, $NPh<\begin{matrix}CS\text{—}NPh\\ |\\ CO\cdot NH\end{matrix}$ or $NPh<\begin{matrix}CS\text{——}NPh\\ |\\ C(OH):N\end{matrix}$, or a mixture of the two forms in equilibrium. It is now shown, however, that these views are incorrect, and that the compound of m. p. 141° is actually 5-thion-1 : 4-diphenylurazole, capable of existing in two forms in equilibrium, whilst the compound of m. p. 219—221° is 5-thiol-1 : 4-diphenylurazole.

By the action of diazomethane and diazoethane on 5-thion-1 : 4-diphenylurazole and 5-thiol-1 : 4-diphenylurazole, compounds are obtained which differ from those produced by the action of alkyl iodides

on the sodium salts of the urazoles. With diazomethane, 5-thion-1 : 4-diphenylurazole yields a *compound*, $C_{15}H_{13}ON_3S$, m. p. 74·5—75·5°, and with diazoethane it furnishes an *ester*, $C_{16}H_{15}ON_3S$, m. p. 79—81°. By the action of diazomethane on 5-thiol-1 : 4-diphenylurazole, an *ester*, m. p. 129·5—130·5°, is produced, isomeric with that obtained from the thionurazole. The thiolurazole and diazoethane give an *ester*, m. p. 105·5—107·5°.

It has been found that 5-thion-1 : 4-diphenylurazole and 5-thiol-1 : 4-diphenylurazole yield sodium salts which are reconverted into the respective urazoles on addition of hydrochloric acid. Both salts react with methyl iodide, and the reaction takes place about eighty times as rapidly with the salt of the thiolurazole as with that of the thionurazole. The *methyl* ester of the thionurazole is obtained as a red, viscous oil, which gradually becomes semi-solid. The methyl ester of the thiol compound is identical with that obtained by the action of carbonyl chloride on $\beta\delta$-diphenyl-γ-methylthiosemicarbazide.

The sodium salts have been esterified quantitatively, and a method has been devised for analysing mixtures of the salts or esters depending on the fact that, under certain conditions, the methyl ester of 5-thiol-1 : 4-diphenylurazole is completely hydrolysed by alkali hydroxide in presence of chloroform, whilst that of the thionurazole is but little affected by this treatment.

The sodium salts of the two urazoles are mutually convertible into one another by two apparently reversible unimolecular reactions, the velocity of rearrangement of sodium 5-thion-1 : 4-diphenylurazole being about nine times as great as that of sodium 5-thiol-1 : 4-diphenylurazole. E. G.

5-Hydroxy-1 : 2 : 3-triazole. Theodor Curtius and August Bockmühl (*Ber.*, 1910, 43, 2441—2446).—5-Hydroxy-1 : 2 : 3-triazole,

$$\begin{matrix} N=\!=\!=N \\ | \qquad \quad > NH, \\ CH{:}C(OH) \end{matrix}$$

was prepared by Curtius and Thompson (Abstr., 1907, i, 95) from diazoacetamide, and by Dimroth and Aickelin (Abstr., 1907, i, 159) from ethyl-1-phenyl-5-triazolonecarboxylate. It has now been more closely studied (compare Dimroth, this vol., i, 518). 5-Hydroxytriazole has m. p. 129°; it is a monobasic acid, and forms a colourless, crystalline *potassium* salt and a *hydrazonium* salt, $C_2H_2N_3(ON_2H_5)$, crystallising in needles, m. p. 117°. An ammonium salt could not be prepared; on evaporation to dryness with ammonia, a colourless, crystalline substance was obtained of the same composition as hydroxytriazole, m. p. about 95°. On the addition of bromine water to an aqueous solution of 5-hydroxytriazole, it decomposes, the gas evolved consisting of molecular proportions of nitrogen and carbon monoxide. Probably dibromoglycollic acid (Curtius and Welde, Abstr., 1907, i, 449) is first formed, and decomposes into oxalic acid, which yields carbon monoxide. E. F. A.

Diazoacetylglycinehydrazide and 5-Hydroxy-1 : 2 : 3-triazole 1-acetylhydrazide. Theodor Curtius and Ernst Welde (*Ber.*, 1910, 43, 862—880).—Curtius and Thompson (Abstr., 1906, i, 404, 940;

1907, i, 95) have shown that ethyl diazoacetylglycine yields derivatives of 5-triazolone-1-acetic acid when treated with ammonia or alkali, and the present authors find that hydrazine hydrate reacts similarly with the ester.

Diazoacetylglycinehydrazide, $N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, prepared by boiling hydrazine hydrate with ethyl diazoacetylglycine (for which an improved method of preparation is given) in alcoholic solution, crystallises in yellow, glistening leaflets, which darken at 120° and decompose at 147°; the *benzylidene* derivative,

$$N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh,$$

forms minute, almost colourless needles, m. p. 199—200°, and the iso*propylidene* derivative, $N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CMe_2$, crystallises in bright yellow, glistening leaflets, m. p. 178° (decomp.). When treated with hydrogen chloride in alcoholic solution, the diazo-hydrazide yields *chloroacetylglycinehydrazide hydrochloride*,

$$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2,HCl,$$

a colourless powder, m. p. 168°; the *benzylidene* derivative of the base is a colourless powder, which does not melt at 300°.

When a cold aqueous solution of diazoacetylglycinehydrazide is treated with a trace of sulphuric acid, nitrogen is evolved, and the solution with benzaldehyde furnishes *hydroxyacetylglycinebenzylidene-hydrazide*, $OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh$, crystallising in small, colourless needles, m. p. 143°.

Hydrazonium 5-*hydroxy*-1 : 2 : 3-*triazole*-1-*acetylhydrazide*,

$$\begin{matrix} CH{\cdot}N{=}N \\ \| \\ C(ON_2H_5) \end{matrix}\!\!>\!N{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2,$$

is formed as a by-product in the preparation of diazoacetylglycine-hydrazide, and is obtained in larger yield by heating ethyl diazoacetyl-glycine in more concentrated solution with a greater excess of hydrazine hydrate; it forms pale red, feathery crystals, m. p. 175° (decomp.). The *potassium* (m. p. 245°, decomp.) and *silver* (decomp. 200°) salts are described. The *hydrazonium* salt of 5-hydroxytriazole-1-acetic acid, $C_2HN_3(ON_2H_5){\cdot}CH_2{\cdot}CO_2{\cdot}N_2H_5$ (reddish needles, m. p. 172°), was also prepared.

5-*Hydroxy*-1 : 2 : 3-*triazole*-1-*acetylhydrazide*, $C_4H_7O_2N_5,H_2O$, prepared from the potassium or silver salt, crystallises in colourless, right-angled tablets, m. p. 147°, which are anisotropic; the *hydrochloride*, a colourless powder, m. p. 174° (decomp.), the *benzylidene* derivative,

$$C_2HN_3(OH){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh,$$

m. p. 190° (decomp.), and the iso*propylidene* derivative, m. p. 155—160°, were prepared. J. C. C.

Diazoacetylglycylglycinehydrazide. Theodor Curtius and Thomas Callan (*Ber.*, 1910, 43, 2447—2457).—Curtius and Welde (preceding abstract) have shown that ethyldiazoacetylglycine and hydrazine hydrate yield at first diazoacetylglycinehydrazide, which with a further amount of hydrazine hydrate undergoes rearrangement to the *hydrazonium* salt of 5-hydroxytriazole-1-acetylhydrazide. It is now shown that ethyldiazoacetylglycylglycine forms *diazoacetylglycyl-glycinehydrazide*. This has the properties of a true diazo-compound and also of an acid hydrazide, liberates nitrogen with dilute mineral

acids, and forms a crystalline compound with benzaldehyde. When boiled in aqueous solution, *hydroxyacetylglycylglycinehydrazide*,

$$OH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

is formed. Prolonged boiling of the hydrazide with hydrazine hydrate converts it into a yellow oil, the *hydrazonium* salt of 5-*hydroxytriazole*-1-*acetylglycinehydrazide*, the *benzylidene* derivative of which was obtained crystalline. The triazole derivative is more readily obtained on warming the hydrazide with dilute alcoholic potassium hydroxide, when the *potassium* salt is obtained as a colourless, very hygroscopic substance. The benzylidene derivative of the triazole, as also that of the 5-hydroxytriazole-1-acethydrazide of Curtius and Welde (*loc. cit.*), combines with *p*-toluenediazonium sulphate, forming red- and orange-hued azo-dyes respectively.

Diazoacetylglycylglycinehydrazide,

$$N_2{:}CH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

crystallises in lustrous, yellow needles, aggregated in rosettes, m. p. 167° (decomp.). *Diazoacetylglycylglycinebenzylidenehydrazide* is a yellow, amorphous powder, m. p. 180—181° (decomp.).

Hydroxyacetylglycylglycinehydrazide is a colourless, very soluble powder, which blackens at 230°, decomp. 240°. *Hydroxyacetylglycylglycinebenzylidenehydrazide* forms short, colourless plates, decomp. 240°.

Acetylhydroxyacetylglycylglycinehydrazide,

$$OAc\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

is a colourless, microcrystalline powder, decomp. 180°.

5-*Hydroxytriazole*-1-*acetylglycinehydrazide*,

$$\begin{matrix} N{=}{=}{=}N \\ | \\ CH{:}C(OH) \end{matrix}\!\!>\!N\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2;$$

the *hydrazonium* salt is a colourless oil, soluble in water with a strongly alkaline reaction; the *potassium* salt is a colourless, crystalline mass.

5-*Hydroxytriazole*-1-*acetylglycinebenzylidenehydrazide* is a pale brown, amorphous powder, m. p. 180° (decomp.). It condenses with *p*-toluenediazonium sulphate in dilute sodium hydroxide solution, forming 4-*tolueneazo*-5-*hydroxytriazole*-1-*acetylglycinebenzylidenehydrazide*, which crystallises in small, reddish-brown needles, m. p. 151·5°.

4-*Tolueneazo*-5-*hydroxytriazole*-1-*acetylbenzylidenehydrazide* forms an orange powder, m. p. 149·5° (decomp.). E. F. A.

Transformation of Diazo-hydrazides into Monohalogen Hydrazides and Azoimides. Theodor Curtius and Thomas Callan (*Ber.*, 1910, **43**, 2457—2467).—By the action of gaseous hydrogen chloride on diazoacetylglycinehydrazide, Curtius and Welde (this vol., i, 786) obtained chloroacetylglycinehydrazide hydrochloride. The action of hydrogen bromide and hydrogen iodide has now been studied in a similar manner. The iodine derivative could not be obtained pure, but it condenses with benzaldehyde to form *iodoacetylglycinebenzylidenehydrazide*, $CH_2I\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N{:}CHPh$. Two other compounds are also formed together with the iodo-derivative, the one, formed in small quantity only, has a high melting point, and is probably the symmetrical secondary hydrazide of iodoacetylglycine. The other, $C_6H_{12}O_2N_3I$, crystallises from alcohol in needles; when boiled

with water an ethyl group disappears, and it is supposed that the original compound contains an ethyl group in the hydrazine residue.

When treated with a concentrated aqueous solution of sodium nitrite, the halogen acetylglycinehydrazides are converted into halogen acetylglycineazoimides. These melt and decompose explosively at higher temperatures; they form anilides with aniline, and boiling with alcohol converts them into urethanes.

By the action of hydrogen chloride on diazoacetylglycylglycinehydrazide, a colourless powder, m. p. 172—174°, was obtained, which did not correspond in composition with chloroacetylglycylglycinehydrazide hydrochloride.

Chloroacetylglycineazoimide, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N_3$, crystallises from ether in well-formed, colourless, lustrous plates. The aqueous solution when heated desposits a colourless, insoluble powder, m. p. 184—185°.

Chloroacetylglycineanilide forms centimetre-long, colourless needles, m. p. 170—171°.

Chloroacetylaminomethylurethane, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO_2Et$, crystallises in beautiful plates of silky lustre, m. p. 149—150°.

Bromoacetylglycinehydrazide hydrobromide, prepared by the action of hydrogen bromide on diazoacetylglycinehydrazide in alcoholic solution, is a heavy, crystalline powder, deliquescent in the air, decomp. 115°.

Bromoacetylglycinebenzylidenehydrazide is a colourless, amorphous powder, m. p. 187—190° (decomp.).

Bromoacetylglycineazoimide crystallises from ether in colourless, silky, lustrous plates. It melts and explodes when heated on a spatula.

Bromoacetylglycineanilide crystallises in bunches of intergrown, small needles, m. p. 161—162°.

Bromoacetylaminomethylurethane separates from alcohol in colourless plates, m. p. 154—155°.

Iodoacetylglycinebenzylidenehydrazide was obtained as an almost colourless, amorphous powder, m. p. 177—179°.

Iodoacetylglycineazoimide forms colourless platelets, which melt and explode.

Iodoacetylaminomethylurethane crystallises in well-formed, colourless plates, m. p. 171° (decomp.).

Iodoacetylglycine-ethylhydrazide (?) was obtained in colourless, microscopic needles, m. p. 147—148°. When boiled with water a *residue*, m. p. 102—104° (decomp.), remained, which with benzaldehyde formed the above-described iodoacetylglycinebenzylidenehydrazide.

Iodoacetylglycineamide, $CH_2I\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, prepared by the action of hydrogen iodide on diazoacetylglycineamide, crystallises in glistening, colourless needles and plates, m. p. 173—175°.

E. F. A.

Hydrazidicarboxylhydrazide. Robert Stollé [and, in part, K. O. H. Leverkus and R. Krauch] (*Ber.*, 1910, **43**, 2468—2470 Compare Curtius and Heidenreich, Abstr., 1895, i, 12; 1896, i, 143). —On prolonged boiling of ethyl hydrazidicarboxylate with hydrazine

hydrate in alcoholic solution, the hydrazine salt of hydrazidicarboxylamide separates out. The mother liquors, when shaken with benzaldehyde, yield *dibenzylidenehydrazidicarboxylhydrazide*,

$$CHPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh,$$

crystallising $+H_2O$ in slender plates, m. p. 229°.

Hydrazidicarboxylhydrazide hydrochloride, prepared from the benzylidene compound by heating with hot hydrochloric acid, crystallises in small, glistening prisms, decomp. 203°. The *condensation product* with anisaldehyde has m. p. 218°, that with salicylaldehyde has m. p. 238°. On heating ethylhydrazidicarboxylate with hydrazine hydrate at 70° and evaporating to dryness in a vacuum, *hydrazidicarboxylhydrazide*, $NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, is obtained in monoclinic prisms, m. p. 196°. It reduces ammoniacal silver nitrate in the cold, and Fehling's solution when warmed. The *sulphate* ($+H_2O$) crystallises in strongly refractive prisms, m. p. 210° (decomp.).

Hydrazidicarboxylazoimide has m. p. 146°, and detonates very violently. With aniline in ethereal solution it forms *hydrazidicarboxylanilide*.

Hydrazidicarboxylethylamide crystallises in plates, m. p. 255°. *Hydrazidicarboxylphenylhydrazide* has m. p. 213° (decomp.).

E. F. A.

Stereomeric Azobenzenes. Catherine V. Gortner and Ross Aiken Gortner (*J. Amer. Chem. Soc.*, 1910, **32**, 1294—1296).—Although it is evident from the structural formula of azobenzene that it should be capable of existence in *syn*- and *anti*-modifications, only one form has hitherto been described.

On heating azoxybenzene with iron filings, a distillate was obtained which consisted of a red liquid containing a crystalline substance. On removing the red liquid by means of light petroleum, in which it is readily soluble, a *substance*, m. p. 237° (corr.), was left in the form of light grey needles, representing about 1% of the azoxybenzene used. This substance was not further investigated.

The deep red solution was washed with cold dilute hydrochloric acid and afterwards with water, and was filtered and left to evaporate. In several cases, only ordinary azobenzene, m. p. 68°, crystallising in prisms, was obtained, but, in other cases, a deep red liquid was left, which furnished a stereoisomeride, m. p. 25° (corr.), crystallising in stellate groups of needles. From a mixture of the two isomerides, that melting at 68° may be removed by crystallisation, the new form being left in the mother liquor. The latter modification is probably *syn*-azobenzene. It has been converted into the form melting at 68°, but the reverse change has not been effected. E. G.

Chromoisomerism and Homochromoisomerism of Azophenols. Arthur Hantzsch (*Ber.*, 1910, **43**, 2512—2516).—Anhydrous α-azophenol is green; β-azophenol is dark red (Willstätter and Benz, Abstr., 1907, i, 566). These chromoisomerides, m. p. 216—218° (decomp., corr.), are very similar in physical and chemical properties, like the chromoisomeric nitroanilines (this vol., i, 475). The chromoisomeric α- and β-azophenols each form chromo-

isomeric (yellow, red, and green) alkali salts, which, however, show the same absorption spectra in solution. Also, α- and β-azophenols themselves in solution exhibit the same molecular extinction and the same absorption spectra (the orange tinge of β-azophenol in ether, described by Willstätter, is due to the presence of a little phenylhydrazine). Consequently, the azophenols, and also their salts, form homochromoisomerides in solution. This behaviour, examples of which have hitherto been furnished only by stereoisomerides, is further evidence of the *syn*- and *anti*-configurations of the α- and β-azophenols suggested by Willstätter. C. S.

The Nitration of Diazonium Compounds. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 224387).—The nitration of diazonium salts frequently yields nitrophenolic compounds, but if the diazotisation is effected in somewhat concentrated sulphuric acid and the solution (or suspension) subsequently treated with nitric acid, or a nitrating mixture, the corresponding nitrated diazonium salts are produced. α-Naphthylamine-5-sulphonic acid (23 parts) was dissolved in concentrated sulphuric acid (200 parts) and treated with nitrosylsulphuric acid (13 parts), dissolved in 50 parts of concentrated sulphuric acid, the mixture stirred, and the temperature maintained at 10—20° during several hours; it was then treated with potassium nitrate (11 parts), when the partly separated diazonium compound redissolved, and, on careful dilution, the nitrated product slowly separated in orange-yellow crystals. F. M. G. M.

The Changes Produced by Urea in the Internal Friction and Electrical Conductivity of Protein Solutions. G. Moruzzi (*Biochem. Zeitsch.*, 1910, 28, 97—105).—The addition of urea to a protein solution in small concentration at first produces a decrease of conductivity, for as a non-electrolyte, it lessens the movements of ions. Later, or in the case of greater concentrations within a few minutes, conductivity, rises owing to the formation of ammonia. Ammonia can also be detected by Nessler's reagent. Ammonium cyanate acts in the same way. Protein acts in this way in virtue of its being a pseudo-base. Urea is believed to owe its hæmolytic power, and its capacity to unite with complement, to the liberation of ammonia in fluids which contain protein. W. D. H.

Action of Alkalis on Protein. III. Albrecht Kossel and Fr. Weiss (*Zeitsch. physiol. Chem.*, 1910, 68, 165—169. Compare Abstr., 1909, i, 542).—Gelatin was digested with 0·5*N*-sodium hydroxide solution for seven to nineteen days, then precipitated with tannic acid containing a little sodium chloride (precipitate 1), and the filtrate saturated with sodium chloride (precipitate 2). To remove the sodium chloride from the filtrate, this was precipitated with phosphotungstic acid, the resulting precipitate decomposed with barium hydroxide, and the peptone derivatives precipitated by Kossel's silver nitrate–barium hydroxide method (precipitate 3), and, after removal of silver nitrate, the filtrate was precipitated with phosphotungstic acid, the latter removed, and the filtrate precipitated

with sodium bismuth iodide solution (precipitate 4). The precipitants were removed from each of the four precipitates by making use of acetone solutions, and then the precipitates were hydrolysed with 33 per cent. sulphuric acid. The precipitates before hydrolysis gave glycine, *dl*-ornithine, and *l*-valine. After acid hydrolysis, *dl*-histidine, *dl*-arginine, *d*-lysine, and proline were isolated. The action of alkalis on gelatin is thus similar to its action on clupein. Certain groups of the protein molecule are sensitive to racemisation so long as they are not united as "intraprotein." When the gelatin which has been partly racemised by alkali is subjected to acid hydrolysis, certain groups are racemised and others remain in the active form. The ornithine group especially appears to be readily racemised. J. J. S.

The Amino-acids Obtainable by the Total Hydrolysis of Proteins. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1910, **68**, 477—486).—A general account of the methods adopted and results obtained by the author and others is given. The paper also contains some new details of analytical results, and replies to criticisms. W. D. H.

The Behaviour of Commercial Egg-albumin to Hydriodic Acid. Theodor Weyl (*Zeitsch. physiol. Chem.*, 1910, **68**, 236—242). —The name *iodalbose* is given to the product obtained by the action of hydriodic acid on egg-albumin; the iodine is firmly held, and the passage of ammonia through an alcoholic solution of iodalbose still leaves an iodine containing residue which differs from iodalbose mainly in containing less carbon; it is termed apo*iodalbose*. By treatment with zinc, an iodine-free substance, *redalbose*, is obtained, which resembles the original egg-albumin closely in composition. Elementary analyses are given throughout. W. D. H.

The Union of Iodine in Iodothyreoglobulin. Adolf Oswald (*Arch. exp. Path. Pharm.*, 1910, **63**, 263—269. Compare Abstr., 1909, i, 123).—All hydrolytic agencies (boiling with acids or alkalis, action of the enzymes trypsin, erepsin, autolase) split off iodine from iodothyreoglobulin in an ionised condition as soon as the protein molecule is broken up into its final cleavage products. A part of the molecule is easily decomposed in this way, and readily yields up its iodine; another part is more resistant. W. D. H.

Hordein and Bynin. A Contribution to our Knowledge of the Alcoholic Extracts of Barley and Malt Albumin. Wilhelm Kraft (*Zeitsch. ges. Brauwesen*, 1910, **33**, 193—195. Compare Abstr., 1907, i, 666; 1908, i, 69).—An account of experiments on the extraction and reactions of hordein and bynin as obtained from malt and barley meal.

Methods of analysis, by hydrolysis and estimation of the decomposition products, are described, and the results compared with those obtained by Osborne and other workers; the two substances were found to resemble each other very closely, but the great difficulty of obtaining them pure rendered the interpretation of results very difficult. F. M. G. M.

Thrombin, Antithrombin, and Prothrombin. William H. Howell (*Amer. J. Physiol.*, 1910, 26, 453—473).—Thrombin was prepared by extracting washed fibrin with 8% sodium chloride solution, and then precipitating coagulable protein with chloroform. It is soluble in water, is not coagulated by boiling in neutral solutions, it gives the majority of the protein colour tests, and contains no phosphorus or sulphur. When allowed to remain in solution, especially at a high temperature, it gradually loses its power of coagulating fibrinogen. If putrefaction occurs, its coagulating power is at first increased and then lost. Saline solutions may be boiled without losing completely their coagulating power; dialysed solutions are more rapidly and completely destroyed by high temperatures. It keeps indefinitely when dried. Increasing amounts of thrombin give increasing amounts of fibrin, although in decreasing proportion. The weight of fibrin produced by a given submaximal amount of thrombin is not affected by the time during which the thrombin is allowed to act.

The conclusion drawn is that thrombin is probably not an enzyme. One part of thrombin can convert at least two hundred and fifteen times its weight of fibrinogen into fibrin. In the non-coagulable "peptone plasma" of the dog, it is antithrombin which prevents the action of thrombin. This anti-substance is destroyed at 75—80°, but not at 60°. Dilution with water causes spontaneous coagulation in "peptone plasma"; dilution with normal saline solution has no such effect. Prothrombin can be converted into thrombin in solutions free from calcium salts. One experiment is recorded of intravenous injection of large quantities of thrombin; no result followed. W. D. H.

New Method for the Preparation of Crystals of Blood Colouring Matter. J. Offringa (*Biochem. Zeitsch.*, 1910, 28, 106—111).—Methods previously employed for the preparation of pure hæmoglobin involve the action of heat, solvents, etc., on the blood. The author believes that these processes are not without influence on the labile hæmoglobin, and in any case crystal formation is very slow. He therefore mixes the corpuscles with kieselguhr, and submits the mass to hydraulic pressure. A fairly concentrated hæmoglobin solution is thus obtained, which, in the case of horse-blood, is frozen solid and centrifugalised until again fluid, when a fair crop of crystals is left. The solution from pig's blood required previous concentration in an air current. The purity of the crystals was established by measurement of the extinction coefficients with the spectrophotometer. In each case the ratio 1·59 was obtained, agreeing closely with the Hüfner figure, 1·578, for oxyhæmoglobin. C. D.

The Refractive Indices of Solutions of Certain Proteins. II. The Paranucleins. T. Brailsford Robertson (*J. Biol. Chem.*, 1910, 8, 287—296. Compare this vol., i, 526).—The collective term paranuclein is applied to an insoluble substance which results from the incomplete peptic hydrolysis of casein, and also to the substance which is formed by high concentrations of pepsin from the synthetic products of complete casein hydrolysis. Additional confirmation of

the view that the substances are identical is obtained by a study of their refractive indices (this vol., i, 526), the value of a being 0·0014.

W. D. H.

Comparative Investigation on the Composition and Cleavage Products of Different Silks. X. Monoamino-acids of the Cocoon of the Italian Silk-worm. GEORG ROOSE. **XI. The Monoamino-acids of the Cocoon of the Japanese Silk "Haruko."** AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1910, 68, 273—274, 275—276).—The following table gives the results in percentages with the two kinds of cocoon (freed from "gum") employed, calculated on the ash-free substance.

	Italian.	Japanese.
Glycine	33·5	35·0
Alanine	20·0	22·6
Leucine	0·75	0·7
Serine	1·9	0·7
Aspartic acid	1·0	1·0
Glutamic acid	0·25	0·07
Phenylalanine	1·2	1·3
Tyrosine	9·0	9·7
Proline	0·8	0·7

W. D. H.

Partial Hydrolysis of Proteins. II. Fibrinheteroproteose. PHŒBUS A. LEVENE, DONALD D. VAN SLYKE, and F. J. BIRCHARD (*J. Biol. Chem.*, 1910, 8, 269—284).—Heteroproteose was prepared from fibrin by a combination of Kühne's and Pick's methods; it contained C 49·52%; H 6·64%, and N 16·46%, which figures agree very well with Pick's. The results of hydrolysis in parts % are as follows:

Glutamic acid	9·51	Aspartic acid	4·73
Leucine	3·05	Glycine	0·15
*iso*Leucine	2·96	Tyrosine	3·48
Valine	3·54	Arginine	6·35
Alanine	3·39	Histidine	1·76
Valine-alanine mixture	1·86	Lysine	4·80
Proline	4·27	Cystine	4·10
Phenylalanine	2·45	Ammonia	1·65
		Total	58·05

W. D. H.

The Study of Enzymes by means of the Synthetical Polypeptides. ARTHUR H. KOELKER (*J. Biol. Chem.*, 1910, 8, 145—175).—*r*-Alanylglycine can be used with great accuracy for the study of proteolytic enzymes, using the optical method. Solutions of *d*-alanyl-*d*-alanine and of *r*-alanylglycine remain unchanged in solution at 15—20° for thirteen months if toluene is used as a preservative. Buchner's grinding method yields the most active enzymes; precipitation with alcohol cannot be used with advantage in the purification of the active principle. The active principle of yeast which hydrolyses alanylglycine dialyses through parchment. The

solution of the enzyme, freed from most of the solids by dialysis, can be evaporated to dryness and redissolved without impairing its activity. The enzyme is still present after thirteen days' digestion at 37°; heating to 75° for a few minutes destroys it completely. Sodium chloride has no influence on the rate of hydrolysis; calcium chloride in concentration 0·1% increases, and in concentration 1% inhibits, the hydrolysis. W. D. H.

Isoelectric Constant of Pepsin. Leonor Michaelis and Heinrich Davidsohn (*Biochem. Zeitsch.*, 1910, 28, 1—6).—From electrometric measurements of the changes in the hydrogen-ion concentration which are brought about by the passage of a current through solutions of pepsin containing hydrogen ions in gradually diminishing quantities, the authors have obtained the so-called isoelectric constant of pepsin. This is the hydrogen-ion concentration for which the positive and negative ions of the amphoteric electrolyte are equal, and the sum of the ions has a minimum value. The value found is $5·5 \times 10^{-3}$. For hydrogen-ion concentrations greater than this, the pepsin migrates to the cathode, and for smaller concentrations towards the anode. If the acidity is much greater than that corresponding with the isoelectric constant, the same effect is found as in the neighbourhood of the isoelectric point. This is attributed in the case of hydrochloric acid solutions to the formation of undissociated pepsinium chloride in presence of the excess of acid. H. M. D.

Action of Pepsin and Hydrochloric Acid. Emil Abderhalden and Eugen Steinbeck (*Zeitsch. physiol. Chem.*, 1910, 68, 293—311).—Gastric juice and hydrochloric acid of the same strength were allowed to act on peptone from various sources, and the result estimated polarimetrically; no change was produced in times varying from one to 170 hours. In similar experiments on native proteins after treatment with gastric juice or hydrochloric acid alone of the same concentration, no effect was observed in either case by the optical method. When solid, denaturalised protein was employed; hydrochloric acid alone produced little or no effect, but gastric juice caused a rise in rotation. If the solidified protein is placed for a short time in gastric juice, washed, and then placed in distilled water, the water after a time at 37° showed evidence of the presence of peptone by the biuret reaction and the polarimeter. W. D. H.

The Action of Sodium Fluoride on Pepsin and Trypsin. Albert J. J. Vandevelde and Edm. Poppe (*Biochem. Zeitsch.*, 1910, 28, 134—137).—Amberg and Loevenhart showed that fluorides retard the action of lipase (Abstr., 1908, i, 235), but in the concentrations used they have no effect on the digestive activity of pepsin and trypsin. W. D. H.

Leucoprotease and Anti-leucoprotease. C. H. Burton Bradley (*J. Hygiene*, 1910, 10, 209—230).—Lympho-protease is a pepsin-like enzyme associated with mono-nuclear leucocytes. Leucoprotease is a trypsin-like enzyme associated with polynuclear leuco-

cytes, and was in the present experiments obtained from pus cells. Experiments on its rate of action are given. It acts only in neutral or faintly alkaline media. The anti-tryptic action of serum varies in different animals, and in the same animal under different conditions (disease, etc.). In the present experiments, the variation in mammals was slight, and immunisation with leucoprotease caused only a small increase of anti-tryptic activity. Goats were the animals used.

W. D. H.

The Erepsin of the Cabbage (Brassica oleracea). Alice F. Blood (*J. Biol. Chem.*, 1910, 8, 215—226).—An active solution of a vegetable erepsin can be prepared from the cabbage by the ammonium sulphate method; the solution deteriorates very slowly if kept cool. It splits off tryptophan from Witte's peptone and from casein, and tyrosine from "peptone Roche." It clots milk and liquefies gelatin. It does not digest fibrin, egg-white, or edestin in neutral, acid, or alkaline media, or in the presence of hydrocyanic acid. It is active over a considerable range of acidity and alkalinity, but is inhibited by a concentration of hydrogen ions corresponding with the acidity of methyl-orange. W. D. H.

Some Peculiarities of the Proteolytic Activity of Papain. Lafayette B. Mendel and Alice F. Blood (*J. Biol. Chem.*, 1910, 8, 177—214).—The digestion of Witte's peptone by papain in the presence of the common antiseptics, judged by the tryptophan test, is very slow. Hydrocyanic acid, however, as Vines pointed out, accelerates proteolysis. The same accelerating effect is noticed when other proteins are digested by papain; it also accelerates the clotting of milk and liquefaction of gelatin. Whether there is more than one enzyme in papain is discussed. Hydrogen sulphide also accelerates the digestion. Hydrocyanic acid is provisionally placed with the co-enzymes. Another peculiarity of papain digestion is that digestion proceeds rapidly even after mixtures of the protein and enzyme have been boiled, and plant proteins are rapidly digested at 80°. Spontaneous deterioration occurs rapidly in solutions of papain; egg-white protects papain in some measure. Extracts of *Ascaris*, which are strongly antipeptic and anti-tryptic, exert no inhibition over papain proteolysis.

W. D. H.

Chemical Composition and Formation of Enzymes. II. Hans Euler and Beth af Ugglas (*Arkiv. Kem. Min. Geol.*, 1910, 3, No. 34, 1—12. Compare this vol., i, 345).—I. *Variation of Enzyme Content of Brewer's Yeast.*—No difference was found in the amount of invertase extracted from yeast dried (1) by treatment with absolute alcohol, (2) by treatment with 95% alcohol, (3) by drying in a vacuum at 40°, and (4) dried at 40° and subsequently slowly heated up to 80°. Yeast cultivated for several generations on dextrose-peptone contained about half as much invertase as the same yeast cultivated in sucrose-peptone. A yeast kept some days under toluene water and subsequently dried, had a low inverting power; the same yeast kept in yeast water and 0·5% sucrose, and strongly aerated, had a normal inverting power.

The diastatic power of barley corns germinated in the one case on moist sand, and in the other on sand moistened with $N/10$-disodium phosphate solution, was in the ratio 1 : 2·3. The increase is attributed to the formation of a co-enzyme from the absorbed phosphate.

II. *Adsorption of Nitrogenous Substances.*—Iron and aluminium hydroxides adsorb proteins, but are not suited for the separation of protein and peptone. Charcoal entirely adsorbs peptone from solution, whilst from yeast extract it adsorbs both nitrogenous and nitrogen-free compounds. From erythrodextrin solutions about 90% is adsorbed by charcoal. Pectic acid is hardly adsorbed by kaolin, strongly by charcoal. Kaolin adsorbs the carbohydrates from yeast-extract preferentially to the nitrogen compounds. The peptones may be removed by charcoal, but the larger part of the nitrogenous constituents still remains. E. F. A.

Inversion of Sucrose by Invertase. V. Destruction of Invertase by Acids, Alkalis, and Hot Water. C. S. Hudson and H. S. Paine (*J. Amer. Chem. Soc.*, 1910, **32**, 985—989).—It has been shown in an earlier paper (this vol., i, 601) that invertase is destroyed by both acids and alkalis at 30°; in each case, the destruction begins at a concentration of about $0{\cdot}01N$, and becomes almost instantaneous at about $0{\cdot}05N$. It is now found that as the temperature is raised, the rate of destruction by acids and alkalis increases, and that at about 60° water itself slowly destroys the enzyme, and at 65° the destruction is quite rapid. The destruction of invertase by hot water is evidently due to the same cause as its destruction by acids and alkalis, namely, the hydrolysis of the complex enzyme molecule. The rates of destruction in the same medium at different temperatures are compared, and the coefficients of the rates of increase for 10° rise of temperature are recorded. The average value of this coefficient is 3·1, which agrees with the general observation that this factor for most chemical reactions is between 2 and 4. The hydrolytic destruction of invertase by acids, alkalis, and hot water thus accords with the common types of chemical reactions.

It is shown that lævulose has a remarkable power of protecting invertase from destruction. The rate of destruction by $0{\cdot}04N$-hydrochloric acid, $0{\cdot}03N$-sodium hydroxide, 50% alcohol, and hot water was first determined in the absence of the sugar and then with it present in concentrations of 2·7, 5·4, and 10·9%. The results are tabulated and plotted as a curve. This protective action of lævulose can be best explained by assuming that the enzyme forms a compound with the sugar which is more resistant to the action of acids, alkalis, hot water, and alcohol than is invertase itself. E. G.

Inversion of Sucrose by Invertase. VI. Theory of the Influence of Acids and Alkalis on the Activity of Invertase. C. S. Hudson (*J. Amer. Chem. Soc.*, 1910, **32**, 1220—1222).—It has been shown in earlier papers (this vol., i, 601; preceding abstract) that invertase is inactive in alkaline solutions, whilst in presence of dilute acids the activity rises to a maximum and afterwards decreases

with increasing acidity. These phenomena are most readily explained on the assumption that acids and alkalis combine with invertase in accordance with the law of mass-action, and thus prevent it from effecting the inversion of sucrose. On this hypothesis, a formula has been deduced by means of which the activity of invertase has been calculated over a considerable range of acidity and alkalinity. The results thus obtained agree closely with the observed activities.

E. G.

Inversion of Sucrose by Invertase. VII. Effect of Alcohol on Invertase. C. S. Hudson and H. S. Paine (*J. Amer. Chem. Soc.*, 1910, **32**, 1350—1357).—The work described in this paper was carried out with the object of ascertaining the influence of alcohol of various concentrations on invertase at 30°. The observation of O'Sullivan and Tompson (Trans., 1890, **77**, 927), that the activity of invertase is reduced by alcohol, is confirmed, and it is found that the relation between the strength of the alcohol and the activity of the enzyme may be represented as a logarithmic or hyperbolic function.

Invertase is destroyed by alcohol of certain strengths. The destruction follows the course of unimolecular reactions; it is not appreciable if the alcohol is under 20%, is almost instantaneous at 50%, and then decreases to nearly zero at 80%. The rate of destruction is greatly retarded by the presence of sucrose, 6% of the sugar reducing the rate in 50% alcohol to about 1% of its original value. An equation is given expressing the rate of inversion of sucrose by invertase in presence of sufficient alcohol to effect the slow destruction of the enzyme, and is found to yield results agreeing closely with those obtained by experiment. In this way the activity of invertase has been determined in 50% and 60% alcohol.

Invertase can be precipitated by alcohol of about 90% strength without much being destroyed, and a preparation has been thus obtained with 78% of the activity of the original solution. In presence of sucrose very little invertase is destroyed, even when precipitated with 70% alcohol; by this method the enzyme has been recovered with 94—96% of the original activity. E. G.

The Invertase of Malt Extracts. Albert J. J. Vandevelde (*Biochem. Zeitsch.*, 1910, **28**, 131—133).—The extract of green malt inverts sucrose. Illustrative experiments are given. W. D. H.

Existence of a Specific Methylglucase in Beer Yeast. Bresson (*Compt. rend.*, 1910, **151**, 485—487. Compare Bierry, Abstr., 1909, ii, 747).—Top-fermentation yeast hydrolyses α-methylglucose, whilst bottom-fermentation yeast does not. The author considers that an extract of the former contains a specific diastase not identical with invertin or maltase. W. O. W.

Preparation of the Polypeptolytic Ferment of Yeast. A. H. Koelker (*Zeitsch. physiol. Chem.*, 1910, **67**, 297—303).—Whilst the filtered liquid obtained from yeast after treatment with chloro-

form very rapidly causes the hydrolysis of sucrose, it was found that alanylglycine is very slowly hydrolysed by the liquid, which is distinctly acid. When, however, calcium carbonate is added, much carbon dioxide is given off, and the liquid becomes very active, far more so than freshly-prepared expressed yeast.

The liquid is prepared by intimately mixing yeast (500 grams) and precipitated calcium carbonate (30 grams) and adding chloroform (30 c.c.). The yeast liquefies in one to three hours, and is then left for three to four days at the ordinary temperature and filtered. After treating with toluene, it is kept at 38° for auto-digestion until the rotatory power becomes constant (ten to forty hours). When filtered it is ready for use.

Calcium chloride does not increase the hydrolytic activity.

N. H. J. M.

Amylase (Diastase). Alfred Wohl and E. Glimm (*Biochem. Zeitsch.*, 1910, 27, 349—375).—The results of experiments on the effect of maltose and other sugars in checking the production of sugar from starch by amylase showed that the union of sugar with the enzyme increases with the concentration of the solution, and is sufficiently complete in 15% maltose solutions to render the production of sugar inappreciable. Similar results were obtained with 10% dextrose solutions, whilst 15% dextrin solution only reduced the activity of amylase to 25%. Galactose (20%) reduced the action by only one-third, and mannose (10%) by only 15%, whilst sucrose and lævulose had no effect.

Addition of 10% of maltose to solutions of amylase enables the latter to retain its enzymatic power when heated at 60° for ten minutes. The same effect is obtained by addition of 20% of dextrose, invert-sugar, and dextrin, whilst sucrose and starch have less effect. In each case the protective action depends on the concentration, and not on the absolute amount of the substance added.

N. H. J. M.

Amylases. II. Action of Pancreatic Amylase. E. C. Kendall and Henry C. Sherman (*J. Amer. Chem. Soc.*, 1910, 32, 1087—1105. Compare this vol., ii, 1011).—A study of the effect of electrolytes and of the concentration of starch on the amylolytic activity of pancreatin. The best commercial preparations are without action on pure starch, but are activated by the addition of neutral electrolytes, or, better, by the action of both a salt and alkali. Below the concentration for maximum activation, the optimum concentrations of salt and alkali depend on each other; above this concentration the optimum for the alkali depends chiefly on the concentration of the starch. Under these conditions, the initial rate of hydrolysis is independent of the amount of starch, but the rate diminishes as the reaction proceeds, the less rapidly the greater the amount of starch present. Equilibrium is attained in 1% starch solutions when the weight of maltose is about 85% of the initial weight of starch. Between 20° and 40°, the temperature-coefficient for amylase conforms to van't Hoff's rule for normal chemical reactions.

Apart from its action as an alkali, asparagine has little effect as an activating agent. W. O. W.

Individuality of Cellase and Emulsin. Gabriel Bertrand and A. Compton (*Compt. rend.*, 1910, 151, 402—404. Compare this vol., i, 212, 290).—Previous experiments not having definitely established the non-identity of cellase and emulsin, a number of comparative observations have been made on the diastases extracted from almonds, maize, and bran. In each case the material was allowed to act on cellose and on amygdalin, when it was found that the ratio between the rates at which these substances underwent hydrolysis varied very considerably according to the source of the enzymes. It would appear, therefore, that cellase and emulsin are two specific enzymes occurring together in plants in variable proportions. W. O. W.

δ-Emulsin. Leopold Rosenthaler (*Biochem. Zeitsch.*, 1910, 28, 408—412. Compare this vol., i, 403).—The action of emulsin on amygdalin occurs in three stages: in the first, mandelonitrile-glucoside and α-dextrose are formed; in the second, the first-named substance yields mandelonitrile (*d*-benzaldehyde cyanohydrin) and β-dextrose; in the third stage, the first-named substance splits up into benzaldehyde and hydrogen cyanide. The first two stages are hydrolytic, the third is not, and the enzyme responsible for the splitting of the nitrile (oxynitrilase) is distinct from that concerned in hydrolysis (glucosidase). Complete saturation with magnesium sulphate and filtration leads to the appearance in the filtrate of the hydrolytic enzyme only. In precipitation with copper sulphate and half saturation with ammonium sulphate, the filtrate contains both enzymes. The action of oxynitrilase is reversible. W. D. H.

Lipase Reactions. Harold C. Bradley (*J. Biol. Chem.*, 1910, 8, 251—264).—When water is present in excess, the hydrolysis of triolein is regularly increased by an increase of lipase; this suggests a mass effect of lipase on the equilibrium of the reaction. A given amount of lipase can under optimum conditions liberate a definite amount of fatty acid from triolein irrespective of the mass of the latter. If more than 50% of water is present, reversion is negligible. Reversion is only appreciable in conditions approaching desiccation. It is possible that lipase, while important in the hydrolysis and absorption of fats, is not important as a factor in their synthesis and storage in the cell. W. D. H.

Action of Acids in the Enzymic Decomposition of Oil by Castor Oil Seeds. Yoshio Tanaka (*J. Coll. Eng. Tōkyō*, 1910, 5, 25—42. Compare Armstrong, Abstr., 1906, i, 126).—Castor oil seeds only hydrolyse fats after acid is added. The absolute quantity of the added acid is the important factor, its concentration having no marked influence. The optimum amount of acid required is related to the amount of castor oil seeds alone, and not to the quantity of oil. In the case of mineral and strong organic acids, the optimum quantities

are proportional to their equivalent weights, with weaker organic acids they are larger. The optimum quantity of an acid of the acetic series increases the higher the homologue is; the inhibitory action of an acid when present in excess is greater the lower the homologue.

Lipase is present in castor oil seeds in the form of an insoluble zymogen, which is readily converted by dilute acid into the insoluble enzyme. The added acid does not act by acidifying the medium, but by liberating enzyme from its zymogen. After treating castor oil seeds with acid and completely washing out all the acid and soluble matter with water, a residue was obtained which hydrolysed fatty oils in neutral solution. This proves lipase to be insoluble and active in a neutral medium. It is less active in the presence of free acid, and inactive in an alkaline medium. E. F. A.

Filtration of Rennet and Pepsin. Casimir Funk and Albert Niemann (*Zeitsch. physiol. Chem.*, 1910, 68, 263—272).—A complete parallelism between the actions of the two enzymes rennet and pepsin was found; they behaved exactly in the same way in attempts to separate them by Holder's filtration method. W. D. H.

Inactivation of Rennet by Shaking. Signe Schmidt-Nielsen and Sigval Schmidt-Nielsen (*Zeitsch. physiol. Chem.*, 1910, 68, 317—343. Compare this vol., i, 83).—A solution of rennet inactivated by shaking recovers its activity after about an hour. The cause of the inactivation is the concentration of the enzyme on the surface of the froth; on remaining quiet, the former condition of things once more obtains. If the froth is removed after shaking, reactivation does not occur in the residual fluid. There is never a complete return of activity, part of the enzyme disappearing; the non-reversible part of the inactivated rennet increases the longer the shaking is continued; this is regarded as an adsorption phenomenon. W. D. H.

The Milk-curdling and Proteolytic Action of the Gastric Infusion of Ox and Calf and of Natural Gastric Juice. A. Rakoczy (*Zeitsch. physiol. Chem.*, 1910, 68, 421—463).—The milk-curdling enzyme spoken of as chymosin is not identical with pepsin; the former is easily destroyed by incubating at 40° with dilute hydrochloric acid. The two enzymes can also be separated by dialysis, pepsin being almost completely precipitated, whilst the chymosin remains mainly in solution. Chymosin can be extracted from the stomach with water or very dilute hydrochloric acid; a stronger acid then dissolves out the pepsin. The milk-curdling power of gastric juice is due partly to chymosin, partly to pepsin. The amount of the former enzyme lessens with age, so that in the ox the milk-curdling power is due to pepsin alone. Bang's parachymosin is possibly identical with pepsin. W. D. H.

Theory of the Action of Oxydases. Alexis Bach (*Arch. Sci. phys. nat.*, 1910, [iv], 30, 152—164).—A polemical summary of

the rival theories of the action of oxydases of Bertrand and of Bach. Colloidal aluminium hydroxide and, to a less extent, other aluminium salts accelerate the transformation of the red oxidation product, produced by the action of tyrosinase on tyrosine, into black melanin. Laccase acting on pyrogallol produces a yellow coloration; the solution in time becomes reddish-brown, and deposits crystals of purpurogallin The addition of a few drops of a solution of an aluminium salt at the yellow stage greatly facilitates the formation of purpurogallin, and the rate of oxidation is the same in a portion of the solution which was boiled to destroy the oxydase. The influence of metallic salts on oxydases is analogous to that of ferrous sulphate on peroxides; the salts are only enabled to act because the oxydase has formed a peroxide. Inorganic salts are not an integral part of oxydases, and do not constitute their active principle; their function is solely to accelerate the oxidising action of the peroxides formed by the true oxydases. E. F. A.

Peroxydase Character of Oxyhæmoglobin. Jules Wolff and E. de Stoeklin (*Compt. rend.*, 1910, **151**, 483—485. Compare Abstr., 1908, i, 490, 573, ii, 1022; 1909, i, 347).—The authors have indicated previously the resemblance between certain colloidal compounds of iron and the peroxydiastases of vegetable origin. Oxyhæmoglobin is now shown to share this similarity, and it has been found by quantitative experiments on the oxidation of potassium iodide, in the presence of hydrogen peroxide, that its catalytic activity surpasses that of the plant peroxydases. It is extremely sensitive to the influence of other substances in the medium, and loses its activity when the solution is boiled. The best results were obtained in an $N/20$-solution of sodium citrate; small quantities of organic acids inhibit the action.

Oxyhæmoglobin shows the usual reactions with pyrogallol, guaiacol, and quinol. The substance appears to be more active after a second crystallisation than after the first. W. O. W.

Isomerisation of Some Phosphorus Compounds. I. Alexander E. Arbusoff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395—420). —The esters of phosphoric acid of the type $P(OR)_3$ under the catalytic influence of alkyl halides are capable of being isomerised into the ethers of the type $PRO(OR)_2$. A rise in temperature of 10° doubles the velocity of reaction, which is also greatest with alkyl iodides and least with the chlorides.

Ethers of the general formulæ $PR'(OR)_2$ and $PR_2'\cdot OR$ (where R is an aliphatic radicle, and R′ any other aliphatic or aromatic radicle) also undergo isomerisation when treated with alkyl halides, being converted into derivatives of quinquevalent phosphorus, $PRR'O\cdot OR$ and $O{:}PRR_2'$ respectively. The velocity of isomerisation is proportional to the mass or concentration of the catalyst, and to the readiness with which the reacting substance forms intermediate additive products; thus the following is the order of the velocity of isomerisation of some of the substances employed: $PR_2'\cdot OEt$, $PR'(OEt)_2$, $P(OEt)_3$.

Phosphenyl chloride, $PPhCl_2$, was prepared by a modification of Michaelis' method (this Journ., 1873, 1148; 1874, 168), a detailed description and figure of the modified apparatus being given; when this substance is heated in a sealed tube at 300°, diphenylphosphoryl chloride, Ph_2PCl, is obtained, which, on treatment in ethereal solution with sodium ethoxide, furnishes *ethyl diphenylphosphinite*, $PPh_2{\cdot}OEt$, b. p. 179°/14 mm., D_0^0 1·0896; the *additive product* with copper iodide has m. p. 190—191°. As a by-product in the formation of the ester, diphenylphosphinic acid, $PPh_2O{\cdot}OH$, is obtained. Under the catalytic influence of ethyl iodide at the ordinary temperature, the ester is converted quantitatively into diphenylethylphosphine oxide, $O{:}PEtPh_2$.

iso*Propyl diphenylphosphinite*, $PPh_2{\cdot}OPr^{\beta}$, has b. p. 160°/8 mm., D_0^0 1·0925, and forms a crystalline *additive* compound with copper iodide, m. p. 114—115°. iso*Propyl diphenylphosphinate*, $PPh_2O{\cdot}OPr^{\beta}$, m. p. 95—96°, is formed as by-product in the preparation of the ester

On heating at 115° with *iso*propyl iodide, *iso*propyl diphenylphosphinite is quantitatively isomerised into *diphenyl* iso*propylphosphine oxide*, $O{:}PPr^{\beta}Ph_2$, which crystallises in prisms, m. p. 145—146°.

iso*Butyl diphenylphosphinite*, $PPh_2{\cdot}OC_4H_9$, has b. p. 202—203°/11 mm., D_0^{17} 1·0311, and forms a crystalline *additive* compound with copper iodide. In the preparation of the ester, iso*butyl diphenylphosphinate*, $PPh_2O{\cdot}OC_4H_9$, m. p. 77°, and diphenylphosphinic acid are also obtained. *iso*Butyl diphenylphosphinite, when heated at 120° with *iso*butyl iodide, is isomerised to *diphenyl*iso*butylphosphine oxide*, $O{:}PPh_2{\cdot}C_4H_9$, which forms needles, m. p. 137·5—138°.

Diphenylmethylphosphine oxide, $O{:}PMePh_2$, prepared from diphenylphosphoryl chloride and sodium methoxide, crystallises in needles, m. p. 109—110°, and diphenylmethylphosphine is formed as a by-product. The intermediate ester was not obtained, as it isomerises so rapidly. Similarly, *diphenylbenzylphosphine oxide*, m. p. 192—193°, is obtained from diphenylphosphoryl chloride and sodium benzyloxide. Diethyl phenylphosphinite, $PPh(OEt)_2$, in contact with ethyl iodide is isomerised into *ethyl phenylethylphosphinate*, PEtPhO·OEt, b. p. 162—164°/16 mm. On hydrolysis, *phenylethylphosphinic acid*,

PEtPhO·OH,

m. p. 79—80°, is formed, of which the barium and silver salts are described. Z. K.

Preparation of Amino-derivatives of Hydroxyarylarsinic Acids and Their Reduction Products. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 224953. Compare Abstr., 1909, i, 347). —It is found that the therapeutically active hydroxyarylarsinic acids can be nitrated, and subsequently reduced to the corresponding amino-compounds having enhanced medicinal value.

Nitrophenolarsinic acid is prepared by dissolving sodium *p*-hydroxyphenylarsinite (144 parts) in 450 c.c. of concentrated sulphuric acid, and slowly dropping in a mixture of 39 c.c. of nitric acid (D 1·4) with an equal volume of concentrated sulphuric acid, with continual stirring and at a temperature of 0°; the mixture is diluted with 1250 c.c. of

water, from which the product separates as a yellow powder. The *alkali* salts are readily soluble in water, yielding deep yellow solutions.

Aminophenolarsinic acid is prepared by the reduction of the foregoing nitro-compound with either sodium amalgam or sodium hyposulphite; it forms minute prisms or leaflets, which blacken and decompose at about 170°.

Diaminoarsenophenol, a yellow powder, is formed by the energetic reduction of nitrophenolarsinic acid with a large excess of sodium hyposulphite; by oxidation with hydrogen peroxide, it is converted into aminophenolarsinic acid.

Nitro-o-cresolarsinic acid, $OH\cdot C_6H_2Me(NO_2)\cdot AsO_3H_2$, prepared from *o*-cresolarsinic acid, is a yellow, crystalline powder, sparingly soluble in cold, readily in hot, water.

Amino-o-cresolarsinic acid is exceedingly soluble in water.

Diaminoarsenocresol, m. p. 165—167° (decomp.), is sparingly soluble in water and in organic solvents.

Dinitrophenolarsinic acid is prepared by the action of excess of nitric acid (D 1·5) with concentrated sulphuric acid on *p*-hydroxyphenylarsinic acid at a temperature of 15—20°; it forms dark yellow leaflets, sparingly soluble in cold, readily in hot, water.

Diaminophenolarsinic acid, silver grey needles, decomposes at about 170° without fusion.

Tetraminoarsenophenol, a bright yellow powder which blackens and decomposes at about 155—157°, is obtained by the reduction of dinitrophenolarsinic acid with a large excess of sodium hyposulphite.

F. M. G. M.

Preparation of Pyrimidine Derivatives containing Mercury. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 224491).—When the alkali salt of 4-imino-2:6-diketodihydropyrimidine-3-acetic acid, $CO<^{NH\text{----}CO}_{CH_2\cdot C(:NH)}>N\cdot CH_2\cdot CO_2Na$, is shaken in aqueous suspension with freshly precipitated mercuric oxide or mercury acetamide during several hours, the solution filtered, concentrated in a vacuum, and treated with alcohol, a *compound*,

$$CO<^{NH\text{----}CO}_{CHg\cdot C(:NH)}>N\cdot CH_2\cdot CO_2Na,$$

is obtained. It is insoluble in organic solvents, but readily soluble in water, and from which mercury is not precipitated on the addition of sodium carbonate.

F. M. G. M.

Organic Chemistry.

Molecular Rearrangements of Carbon Compounds. C. G. Derick (*J. Amer. Chem. Soc.*, 1910, **32**, 1333—1350).—A general paper of a theoretical character, dealing especially with rearrangements of the non-reversible type, such as the transformation of Δ^{β}-unsaturated acids into their Δ^{α}-isomerides. A discussion is given of the formation, stability, and velocity of rearrangement of compounds of this class, and a system of classification of molecular rearrangements of organic compounds is presented. E. G.

Wax Oil. Thor Ekecrantz and E. Lundström (*Arch. Pharm.*, 1910, **248**, 500—513).—At the present time wax oil (*oleum cerae*) is always prepared by the dry distillation of wax and calcium oxide. The authors have examined wax oil obtained by three different methods: (*A*) pure beeswax and twice its weight of calcium oxide are distilled in an iron retort, the distillate being rectified by two distillations with twice the quantity of calcium oxide; (*B*) equal weights of beeswax and calcium oxide are distilled in a glass retort on a sand-bath, the distillate being rectified by a second distillation with an equal weight of calcium oxide; (*C*) wax oil prepared in an apothecary's laboratory, and guaranteed unadulterated. *A* is a greyish-yellow mass of crystalline leaflets, and has m. p. 34·5°, $D^{34.5}$ 0·792, acid number 15·4, and iodine number 68·3. *B* is a brownish-yellow oil, having D^{20} 0·792, acid number 8·7, and iodine number 84·3. *C* is also a brownish-yellow oil, having D^{20} 0·790, acid number 9·7, and iodine number 86·6. The oils are distilled with steam, and the residues are separated by acetone into a liquid and a solid portion; from the proportions of the liquid volatile with steam, the liquid non-volatile with steam, and the solid, it is evident that in the distillation of wax and calcium oxide the decomposition of the initially-formed products is least in the oil prepared by method *A* and greatest in that prepared by method *B*. The liquid volatile with steam consists chiefly of a mixture of saturated and unsaturated hydrocarbons, containing 10—16 atoms of carbon; the non-volatile liquid, of a similar mixture containing 16—27 atoms of carbon. The solid portion, m. p. 58—59°, iodine number 13·1, is separated by ether into two parts; one, sparingly soluble in ether, consists chiefly of nonocosane and a little myricyl alcohol; the other, easily soluble in the solvent, is probably a mixture of nonacosane, pentacosane, and a small quantity of unsaturated hydrocarbons. Several commercial wax oils have also been examined. The authors state that the sp. gr. of a wax oil should lie between 0·790 and 0·792, the acid number between 8 and 12, and the iodine number between 80 and 90. They recommend that the iodine number should be determined in the liquid constituents which are volatile with steam. C. S.

Additive Power of 2-Pentene [Δ^{β}-Amylene]. Roger F. Brunel and Eugene G. Probeck (*Amer. Chem. J.*, 1910, **44**, 5, 431—438. Compare Michael, Abstr., 1909, i, 197).—A comparison

is given of the additive power of Δ^{β}-amylene towards acid with that of β-methyl-Δ^{β}-butylene and of α-butylene. Michael's hypothesis regarding the relation between the position of atoms in a molecule and their influence on each other is adopted (Abstr., 1900, i, 321; 1906, i, 550). According to this hypothesis, if one of the unsaturated carbon atoms in the molecule be numbered 1, the mutual influence between this atom and the other atoms of the molecule will decrease according to the scale: 2—3—5—6—4—7—(9—10—11)—8.

In the case of Δ^{α}-butylene and Δ^{β}-amylene this gives:

$$\overset{4\ 3\ 2\ 3}{H_3C}\cdot\overset{1\ 2}{CH_2}\cdot\overset{2\ 3}{CH}:\overset{1\ 2}{CH_2} \qquad \overset{3\ 2\ 1\ 2\ 2\ 3\ 3\ 4}{H_3C}\cdot\overset{4\ 5}{CH}:\overset{4\ 3\ 2\ 3\ 1\ 2\ 2\ 3\ 3\ 4}{CH}\cdot CH_2\cdot CH_3.$$
$$\underset{5\ 4\ 3\ 4}{\qquad}\ \underset{2\ 3\ 1\ 2}{\qquad} \qquad \underset{\qquad}{\qquad}$$

By an additive process the unsaturated atoms in each molecule are compared, and it is shown that from this consideration alone, the greater additive power should be found in the case of Δ^{β}-amylene, although the difference should not be great. As, however, with the transition from the C_4 to the C_5 series the reduction in the affinity for hydrogen increases, there is a possibility that Δ^{β}-amylene may show the weaker additive power. This is found experimentally to be the case, the ratio being about 7 : 5. A similar comparison with β-methyl-Δ^{β}-butylene shows that the difference in additive power in this case must only depend on the degree of attraction of the negative radicles. Experimentally the velocity with which β-methyl-Δ^{β}-butylene dissolves in dilute sulphuric acid is over one hundred times as great as for Δ^{β}-amylene. N. C.

The Adsorption of Acetylene by Colloidal Palladium. Carl Paal and Christian Hohenegger (*Ber.*, 1910, 43, 2684—2692).—The liquid hydrosol of palladium, prepared according to the method of Paal and Amberger, dissolves considerable quantities of acetylene. The determination of the amount adsorbed was made in a way similar to that used by Paal and Gerum (Abstr., 1908, ii, 392) to measure the adsorption of hydrogen.

Several days are necessary before the adsorption is complete. After adsorption is complete at room temperature, warming at 40—70°, accompanied by the exercise of a slight pressure, increases the amount of acetylene adsorbed. This extra acetylene is not liberated when the original temperature and pressure are restored, since it is converted partially into volatile and non-volatile condensation and polymerisation products, which, however, could not be isolated in sufficient quantity for identification.

On exposing a palladium hydrosol which has been saturated with acetylene to the air, the chemically unchanged acetylene is set free, especially on warming. On bringing the palladium sol again into contact with acetylene, very little gas is adsorbed, probably because the palladium particles are coated with the acetylene condensation products. This is also the case when the palladium sol is extracted with ether, acidified in order to precipitate the adsorption compound of the solid palladium sol with free protalbic acid, and the precipitate again converted into a liquid sol by the addition of water containing a little sodium hydroxide.

The number of molecules of acetylene adsorbed per gram-atom of

palladium varied from 0·44 to 1·90 molecules, namely, from 1075 to 4690 volumes of acetylene per one volume of palladium, depending on the duration of the experiment and the concentration of the palladium.

T. S. P.

The Adsorption of Acetylene by Palladium Black. Carl Paal and Christian Hohenegger (*Ber.*, 1910, 43, 2692—2694).—The adsorption of acetylene by palladium black was measured in an apparatus similar to that used by Paal and Gerum (Abstr., 1908, ii, 392) to determine the adsorption of hydrogen. The palladium was suspended either in an aqueous solution of sodium protalbate or in an aqueous solution of ammonia, or in aqueous alcohol, in order to determine whether the acetylene adsorbed by the palladium reacted with the dissolved substances. In all three cases, approximately equal quantities of acetylene were adsorbed (1·36—1·53 molecules per gram-atom of palladium); in no case did the adsorption exceed that obtained with colloidal palladium under similar conditions.

Some of the adsorbed acetylene was changed into condensation products, but not to the same extent as with colloidal palladium.

T. S. P.

Tetranitromethane. Ernest Berger (*Compt. rend.*, 1910, 151, 813—815. Compare Pictet and Généquand, Abstr., 1903, i, 305, 596; Chattaway, Trans., 1910, 97, 2099).—The following method is recommended for the preparation of tetranitromethane. A mixture of 160 grams of absolute nitric acid (or 180 grams of fuming nitric acid) with glacial acetic acid (100 grams) is treated, in a flask kept cool under the tap, with acetic anhydride (290 grams). The flask is allowed to remain in cold water for some hours, and then for a night at the ordinary temperature. After heating for three to four hours at 25—30°, the temperature is raised by 5° every three to four hours until it reaches 65—70°, when the liquid is poured into four times its volume of water. The tetranitromethane is washed and dried over anhydrous sodium sulphate; the acid liquid from which it separates contains trinitromethane and trinitroacetic acid. The yield is 28—60 grams, according to the concentration of the nitric acid.

Tetranitromethane has b. p. 21—23°/22 mm., 124—125°/750 mm. with slight decomposition; D^{22} 1·620. The heat of combustion was determined in presence of amyl alcohol, since the compound itself contains too much oxygen. The results are expressed by the equations: $C(NO_2)_4 = CO_2 + 2N_2 + 3O_2 + 89{\cdot}6$ Cal. C diamond $+ 2N_{2(gas)} + 4O_{2(gas)} = C(NO_2)_4 + 4{\cdot}7$ Cal.

W. O. W.

Catalytic Reactions by means of Metallic Oxides. Alphonse Mailhe (*Chem. Zeit.*, 1910, 43, 1173—1174, 1182—1184, 1201—1204).—In these three papers a résumé is given of the results of recent work carried out by the author and others on the catalytic reactions induced by heated metallic oxides. The first paper deals with the decomposition of alcohols, acids, and esters, and records, for the most part, results already published (Senderens, Abstr., 1907, i, 577; 1908, ii, 166; i, 494, 495; 1909, i, 127, 286, 627; and this vol., i, 11, 179, 318, 489; Sabatier and Mailhe, 1908, i, 594, 713; 1909, i, 546, and this vol., i, 294, 606). In the second paper a theory of these catalyses already outlined (*loc. cit.*, but especially 1908, i, 594, and this vol., i,

294) is discussed in detail in its application to various special cases, and the preparation of amines is described (Abstr., 1909, i, 292), with a number of new examples of the application of the process to this class of compounds. The third paper deals with the preparation and decomposition of thiols by this process (this vol., i, 294, 456, 536).

T. A. H.

Two Active Alcohols and a Third Ketone Contained in Cocoanut Oil. Albin Haller and A. Lassieur (*Compt. rend.*, 1910, 151, 697—699. Compare this vol., i, 355).—The odoriferous constituents of the "essence" of cocoanut butter have been shown previously to consist of higher fatty acids with neutral substances. The latter have now been separated into alcohols and ketones by means of phthalic anhydride. The alcoholic portion consists chiefly of d-*methylnonylcarbinol*, b. p. 228—233°, D_4^{23} 0·827, n_{23} 1·4336, $[\alpha]_D$ + 1°24′, with a small quantity of d-*methylheptylcarbinol*, b. p. 195—196°, D_4^{25} 0·823, n_{21} 1·4249, $[\alpha]_D$ + 2°25′. The ketonic portion contains about 75% of methyl nonyl ketone, together with methyl heptyl ketone and methyl undecyl ketone.

W. O. W.

Basic Properties of Oxygen: Compounds with Bromine and Iodine. Douglas McIntosh (*J. Amer. Chem. Soc.*, 1910, 32, 1330—1333).—It has been suggested by Tschelinzeff and Konowaloff (Abstr., 1909, i, 353) that the compound $C_4H_{10}OBr_2$, obtained by the action of bromine on ethyl ether, has the constitution $C_4H_{10}O<^{Br}_{Br}$.

It is now stated that the compound obtained by these authors was not pure, and that the value of the molecular weight in acetic acid which they obtained is not trustworthy, since the dibromide is decomposed by this solvent. Attempts have been made to determine the molecular weight of the di- and tri-bromides of ethyl ether by f.-p. measurements in chloroform solution, but without success, since the substance undergoes partial decomposition under these conditions. It has also been found that this constant cannot be determined by Ramsay and Shields' method.

Waentig (this vol., ii, 117) has stated that iodine combines with certain organic solvents at low temperatures. It is now found that when a solution of iodine in alcohol or acetone is cooled to − 80° or − 90°, a substance separates which may be mistaken for a compound. When completely dried at a low temperature, however, the product is shown by analysis to be iodine, contaminated with a little of the solvent. When ethyl acetate is used, mixed crystals of the solvent and iodine may be obtained.

When bromine and chlorine are dissolved in organic solvents containing oxygen, an appreciable amount of heat is developed, whilst, in the case of iodine, a slight absorption of heat occurs. On the basis of these facts, it is shown that it is improbable that iodine compounds could be produced in a reasonably pure state by cooling the solutions to a low temperature.

E. G.

The Solubilities of the Pharmacopœial Organic Acids and Their Salts. Atherton Seidell (*Bull.* No. 67, *Hyg. Lab., U.S. Pub. Health and Mar. Hosp. Serv.*, 1910, 7—98).—The importance attached

to the quotation of solubility determinations in pharmacopœial descriptions of chemicals has led the author to re-determine the solubilities of the organic acids of the United States Pharmacopeia in water, aqueous alcohol, and a number of common organic solvents, and to obtain like data for the official salts of these acids as regards water and aqueous alcohol. The results obtained, together with obviously trustworthy results recorded by previous investigators, are tabulated, and also represented graphically in the original.

The method used consisted in agitating the solvent with excess of the acid or salt at the selected temperature, due precautions being taken to secure saturation in each case and to ensure uniform experimental conditions. The specific gravity of the saturated solution was determined, and then the quantity of substance in solution ascertained by evaporation to dryness, or if this was impossible, by chemical analysis. The results are expressed as the number of grams of substance in 100 grams of the saturated solution.

The following deductions are drawn from a consideration of all the results obtained. Of the thirty-five substances examined, only nine gave results showing satisfactory agreement with the figures quoted in the U. S. P., the remainder showing differences ranging from 5 to 100%. A solubility determination is of little value as a criterion of the purity of a substance. It is impossible to predict the solubility of a substance in a mixture of alcohol and water from a knowledge of its solubility in each of these solvents alone. Citric acid shows nearly parallel solubility curves for the anhydrous and hydrated forms in aqueous alcohol, the second being the more soluble substance. Potassium citrate mixed with aqueous alcohol causes the separation of an upper layer of nearly pure alcohol, and a lower layer of aqueous salt solution (compare Linebarger, Abstr., 1892, 1146). Oleic acid shows apparently unstable solubility equilibrium in aqueous alcohol at certain concentrations. Trichloroacetic acid undergoes partial esterification in aqueous-alcoholic solutions. T. A. H.

Organic Salts of Yttrium. Sebastian Tanatar and I. Voljanski (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 586—590).—Yttrium *propionate*, $(EtCO_2)_3Y$, formed by the prolonged heating on a water-bath of yttrium oxide with dilute propionic acid, can be readily obtained pure by recrystallisation. It forms white, monoclinic needles, and is insoluble in all organic solvents except warm alcohol, by which, however, it is converted into the *basic* salt. The following salts were also obtained: the iso*butyrate*, $(C_3H_7\cdot CO_2)_3Y$; *lactate*, $(OH\cdot CHMe\cdot CO_2)_3Y,4H_2O$; *benzoate*, $Y(OBz)_3$; *fumarate*, $(C_4H_2O_3)_3Y_2,2H_2O$; *phthalate*, $(C_{10}H_4O_4)_3Y_2,C_{10}H_6O_4$; *crotonate*, $(CHMe:CH\cdot CO_2)_3Y,5H_2O$; *malate*, $(C_4H_4O_5)_3Y_2$; and *citroconate*, $(C_5H_4O_4)_3Y_2,9H_2O$.

Yttrium nitrate, $Y(NO_3)_3,2H_2O$, is formed by dissolving yttrium oxide in excess of dilute nitric acid and evaporating to a syrup, which is dried at 100°. After cooling and stirring, the syrup suddenly forms tiny crystals with development of heat. Z. K.

Transformation of Stereoisomeric Ethylenic Compounds. I. Paul Pfeiffer (*Ber.*, 1910, 43, 3039—3048).—When an $\alpha\beta$-dihaloid derivative of butyric or β-phenylpropionic acid is treated with potassium hydroxide, it furnishes the unstable corresponding α-halogenated *iso*crotonic or *allo*cinnamic acid, whereas with pyridine, it yields the stable α-halogenated isomeride. In both cases the unstable form is first produced, but in the presence of pyridine this is transformed into its isomeride.

[With A. Langenberg.]—$\alpha\beta$-Dichlorobutyric acid reacts slowly with pyridine at the ordinary temperature, but more rapidly on warming at 100°, to give α-chlorocrotonic acid. Under like conditions, $\alpha\beta$-dibromobutyric acid furnishes α-bromocrotonic acid. $\alpha\beta$-Dichloro-β-phenylpropionic acid is not decomposed by pyridine at atmospheric temperature, but at 100° furnishes α-chlorocinnamic acid, whilst $\alpha\beta$-dibromo-β-phenylpropionic acid gives cinnamic with some α-bromocinnamic acid.

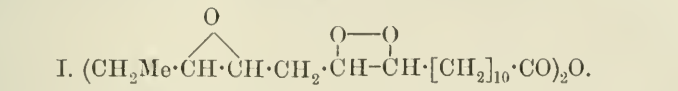
α-Chloro*iso*crotonic acid, when kept in pyridine solution with pyridine hydrochloride at atmospheric temperature, or more rapidly on warming, is converted into α-chlorocrotonic acid, and under like conditions a similar change ensues with α-chloro*allo*cinnamic acid, α-bromo*allo*cinnamic acid, and α-bromo*iso*crotonic acid, the last-mentioned acid being also transformed when kept with pyridine alone. β-Chloro*iso*crotonic acid is not transformed into β-chlorocrotonic acid under these conditions. T. A. H.

Linolenic Acid and Linseed Oil. Ernst Erdmann and Fred Bedford (*Zeitsch. physiol. Chem.*, 1910, 69, 76—84. Compare Abstr., 1909, i, 357).—Several miscalculations are pointed out in Rollett's work (Abstr., 1909, i, 760). The general conclusions drawn are: (1) The hydrogen and iodine numbers show that in linseed oil there is not more than 20—25% of acids, $C_{18}H_{30}O_2$, containing three ethylene linkings. This is mainly α-linolenic acid, which yields a hexabromide, m. p. 179°. (2) When the solid hexabromide is treated with zinc, a mixture of two stereoisomeric acids is formed; 75% of this mixture consists of β-linolenic acid and 25% of the α-acid. The β-acid yields an oily tetrabromide, and this with zinc gives the β-acid together with polymerisation and anhydro-products. (3) Rollett's conclusions that only one linolenic acid is present in linseed oil, and that the amount is some 50—60% are incorrect. J. J. S.

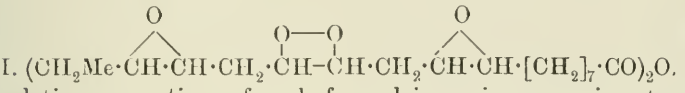
The Composition of Boiled Linseed Oil and the Distribution of Oxygen in Dried Layers of Oil. I. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 658—676. Compare Erdmann, Abstr., 1909, i, 357).—The solid substances formed when linseed oil is dried on a plate contain unsaturated double linkings, and even when the greatest quantity of oxygen has been absorbed, the dried oil still gives an iodine number not less than 14·15. The amount of oxygen absorbed depends on the thickness of the layer and the surrounding temperature, but in all cases if, after the layer has ceased to increase in weight, the surface of the layer be removed, oxygen commences to be absorbed again and the weight increases.

Although fresh linseed oil has no reducing properties, the oil dried on plates is markedly reducing, owing to the formation of two *linoxins* from the glycerides of linolic and linolenic acid.

The linoxin (I) from linolenic acid is a solid insoluble in alcohol and ether, that (II) from linolic acid is a soluble syrupy liquid. The linoxins are not ozonides, and a detailed study of their properties leads to the conclusion that they have the following constitution :



I. $(CH_2Me\cdot CH\cdot CH\cdot CH_2\cdot CH{-}CH\cdot[CH_2]_{10}\cdot CO)_2O$.



II. $(CH_2Me\cdot CH\cdot CH\cdot CH_2\cdot CH{-}CH\cdot CH_2\cdot CH\cdot CH\cdot[CH_2]_7\cdot CO)_2O$.

The relative proportions of each formed in various experiments are estimated and found to agree very well with the theoretically calculated numbers. Z. K.

The Ability of Alcoholic Hydroxyl Groups to Form Complexes. G. Calcagni (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 333—337).—By a method analogous to that of Weinland (Abstr., 1909, i, 757), the author has prepared basic salts of hexaglycollato- and hexalactato-trichrome bases. To them is to be assigned a constitution similar to that of the salts obtained by Weinland, so that in this case the alcoholic hydroxyl groups take part in the formation of the salt, whilst other negative radicles (chlorine, bromine) only strengthen the carboxylic hydrogen. The *basic glycollate* of a *hexaglycollatotrichrome base*, $\left[Cr_3\begin{matrix}(CO_2\cdot CH_2\cdot OH)_6\\(OH)_2\end{matrix}\right]CO_2\cdot CH_2\cdot OH,Cr(OH)_3$, is obtained as a dark green, hygroscopic powder by dissolving chromic hydroxide in glycollic acid and precipitating with alcohol. It is stable towards ammonia and sodium hydroxide; chromic hydroxide is only precipitated after prolonged ebullition with the latter. The *basic lactate* of a *hexalactatotrichrome base*,

$$\left[Cr_3\begin{matrix}(CO_2\cdot CHMe\cdot OH)_6\\(OH)_2\end{matrix}\right]CO_2\cdot CMe\cdot OH,Cr(OH)_3,$$

was obtained in the same way, and has similar properties. The analytical results indicate the presence of about $5H_2O$ in the molecule. When it is treated with fuming nitric acid on the water-bath, only one of the lactate groups is replaced, the *nitrate*,

$$\left[Cr_3\begin{matrix}(CO_2\cdot CHMe\cdot OH)_6\\(OH)_2\end{matrix}\right]NO_3,Cr(OH)_3,$$

being formed. R. V. S.

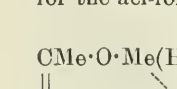
The Equilibrium Isomerism of Acetoacetic Ester and the So-called Isorropesis of its Salts. Arthur Hantzsch (*Ber.*, 1910, 43, 3049—3076).—A systematic investigation of acetoacetic ester and its homologues has been made both by refractometric (compare Brühl, Abstr., 1905, i, 407) and ultra-violet absorption spectra methods, with a view to determining its constitution. The following are the chief results recorded.

The dialkylacetoacetates, which exist only in the ketonic form, absorb but little ultra-violet light, whilst ethyl ethoxycrotonate shows large absorption, but neither of these exhibits much change in absorption in whatever solvent it is examined. Ethyl acetoacetate, on the contrary, shows great variation in absorption, depending on the solvent used; thus, in water and dilute hydrochloric acid, it is slightly absorbent, whilst in indifferent solvents the absorption increases inversely as the dielectric constant of the solvent, and reaches its maximum in hexane. The absorption also increases with rise of temperature and with increasing dilution, the latter especially in hexane. This rise in absorptive capacity is parallel with Brühl's exaltation of refraction. Methyl- and ethyl-acetoacetic esters show similar behaviour. Homogeneous ethyl acetoacetate shows greater absorption than its solutions.

Tables and graphs illustrating these general results are given in the original.

The following explanation of these results is given. The acetoacetates and their mono-substitution products, in the homogeneous state and also in solution in indifferent solvents, are equilibrium mixtures of keto-enolic isomerides. The equilibrium point is shifted to the enol side by (1) rise of temperature, (2) dilution in the same solvent, (3) use of solvents of decreasing dielectric constant. Ethyl acetoacetate is strongly enolised and slightly associated. In dilute hydrochloric acid solution, it is practically entirely ketonised, and in dilute hexane solution almost entirely enolised, since then it shows nearly the same absorption spectrum as ethyl ethoxycrotonate. In water, at medium temperatures, it is about one-fifth, and in methyl alcohol about nine-tenths, enolised. These results are confirmed in part by Stobbe's observations on the ferric chloride test (Abstr., 1907, i, 177).

It is pointed out that the phenomenon of isorropesis (Stewart and Baly, Trans., 1906, 89, 498) is particularly well shown by the addition of alkalis to ethyl acetoacetate (compare Baly and Desch, *ibid.*, 1904, 85, 1036), and is probably the result of "salt" formation, since maximum absorption is reached more quickly the greater the concentration of ester and the more acidic in nature the latter is. Further, the metallic derivatives of ethyl acetoacetate are optically and chemically different from the enol-form of the ester itself, and in these derivatives the ester must exist in a new form, which may be called the aci-form, since it probably also occurs to a minute extent in solutions of the ester in hexane. The relationship of the aci- and enol forms cannot be that of stereoisomerides, as these would be optically identical (this vol., i, 474), and of the formulæ considered for the aci-form, the most likely is the annexed one, the dotted line indicating a "subsidiary valency." This formula represents a "valency isomeride" of the enol form and permits in a modified way of Baly and Desch's "oscillation" explanation of isorropesis, the oscillation taking place by an interchange of "principal" and "subsidiary" linkings at the points marked 1 and 2, with a suitable change in position of the double linkings. Apart from the equilibrium isomerism



between the keto and enol forms and between the enol and aci-forms, there is a third possible equilibrium between the trans-enol and cis-enol forms, and it seems likely that the cis-enol form only can pass into the aci-form thus :

T. A. H.

Ethyl α-Nitroso*iso*heptoate and the Action of Nitrous Gases on Allyl-, Dimethyl-, and Diethyl-acetoacetic Esters. Julius Schmidt and August Haid (*Annalen*, 1910, 377, 23—30. Compare Schmidt and Widmann, Abstr., 1909, i, 453).—The nitrous gases from a mixture of nitric acid and arsenious anhydride react with ethyl *iso*heptoate, yielding *ethyl α-nitroso*iso*heptoate*,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CH(NO)\cdot CO_2Et,$$

as a dark blue oil, $D_4^{20\cdot2}$ 1·054, and $n_D^{20\cdot2}$ 1·6251. It has a strong odour, cannot be distilled even under very low pressures, and gives Liebermann's nitroso-reaction. When kept or when treated with water or alkalis, the blue liquid becomes colourless; this is partly due to polymerisation, and partly to conversion into the isomeric oximino-derivative. It has a deeper colour, and is also somewhat more stable than the analogous *iso*hexoate (Schmidt and Widmann). When oxidised with hydrogen peroxide, the nitroso-ester yields *ethyl α-nitro*iso*heptoate*, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH(NO_2)\cdot CO_2Et$, as a yellow oil, D_4^{15} 1·070, n_D^{15} 1·4486.

The nitrous gases react with ethyl allylacetoacetate, but definite products could not be isolated, and when ethyl dimethyl- and diethyl-acetoacetates were used, the unaltered esters were recovered. It would thus appear that substituted acetoacetic esters, in which both the methylene hydrogens are replaced by alkyl groups, cannot yield nitroso-derivatives. J. J. S.

Esters of Aliphatic Nitroso- and Nitro-carboxylic Acids. Julius Schmidt and Hedwig Dieterle (*Annalen*, 1910, 377, 30—70. Compare Schmidt and Widmann, Abstr., 1909, i, 453; Schmidt and Haid, preceding abstract).—Nitrous gases from arsenious anhydride and nitric acid are able to replace by nitroso-groups, not merely acetyl, but also formyl and benzoyl groups in esters of α-acylated saturated carboxylic acids. The formyl group is replaced most readily, and the benzoyl group least readily. In the last case the reaction requires several days for completion, and the product actually isolated is not a true nitroso-derivative, but the isomeric oximino-compound; at the same time, partial hydrolysis occurs, so that the final product in the case of ethyl benzoylsuccinate is ethyl hydrogen oximinosuccinate, $CO_2H\cdot CH_2\cdot C(:NOH)\cdot CO_2Et$.

The nitro-group in esters of nitro-substituted saturated acids can also be replaced by the nitroso-group by the action of the nitrous gases on the ester in the absence of a solvent, but it has not been found possible, so far, to replace the bromine atom in α-brominated

esters by the nitroso-group. When ethyl formylphenylacetate is used, an oximino-group replaces the formyl group, and at the same time the phenyl radicle is nitrated, so that the final product is

$$NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CO_2Et.$$

Ethyl diacetylacetate does not react with the nitrous gases; the presence of a CH-group in the acylated ester is thus essential for the reaction (compare preceding abstract), and it is probable that the nitroso-group first replaces the hydrogen atom of this group and that hydrolysis then takes place, resulting in the elimination of a molecule of the organic acid, for example: $CH_3\cdot CO\cdot CHR\cdot CO_2Et \longrightarrow CH_3\cdot CO\cdot C(NO)R\cdot CO_2Et \longrightarrow CH_3\cdot CO_2H + NO\cdot CHR\cdot CO_2Et$.

The changes which the nitroso-derivatives undergo when kept have been examined, mainly by cryoscopic measurements. In the case of ethyl α-nitrososuccinate and ethyl α-nitroso-*n*-butyrate, the blue oils undergo polymerisation, yielding the nearly colourless bimolecular products, which, in their turn, change gradually into the yellow or colourless, unimolecular oximino-derivatives, for example:

$$\underset{\text{Blue.}}{CO_2Et\cdot CH_2\cdot CH(NO)\cdot CO_2Et} \longrightarrow \underset{\text{Nearly colourless.}}{[CO_2Et\cdot CH_2\cdot CH(NO)\cdot CO_2Et]_2} \longrightarrow \underset{\text{Yellow.}}{CO_2Et\cdot CH_2\cdot C(:N\cdot OH)\cdot CO_2Et}.$$

In most other cases the second change begins before the first is complete, so that the molecular weight never reaches the value required for the bimolecular compound. This is extremely well shown in the case of ethyl α-nitrosopropionate, prepared from ethyl α-formylpropionate. The conversion into the oximino-compounds is accelerated to an enormous extent by the presence of minute traces of alkalis, and most solvents, for example, water and benzene, also facilitate the transformation.

Good yields of esters of amino-acids cannot be obtained by reducing either the nitroso- or the more stable nitro-esters, the best results being obtained when stannous chloride and hydrochloric acid are used. Small amounts of the oximino-carboxylic acids can be prepared by hydrolysing the esters of the nitroso-acids with very dilute alkali at low temperatures. Small yields of the potassium salts of the α-nitro-acids are formed when the corresponding esters are treated with concentrated potassium hydroxide solution. They form golden-yellow crystals, and cannot be transformed into the corresponding acids.

Ebert's ethyl α-oximinosuccinate (Abstr., 1885, 1122) is formed readily when ethyl α-nitrososuccinate is shaken with sodium carbonate solution; it has n_D^{18} 1·3765, and when hydrolysed with sodium hydroxide, the oximino-ester yields oximinosuccinic acid, ethyl oximinopropionate, or oxalacetic acid, according to the conditions of the experiment, but in all cases the yields are extremely poor, namely, 1 to 2%.

Ethyl α-nitroso-n-*valerate*, $CHEt\cdot CH(NO)\cdot CO_2Et$, prepared from ethyl *n*-propylacetoacetate, forms a dark blue oil, and retains the blue colour for some twelve to twenty-four hours at the ordinary temperature. It has D_4^{20} 1·213 and n_D^{20} 1·4350, and the isomeric α-oximino-ester is a yellow oil, with n_D^{18} 1·3250. When oxidised with hydrogen peroxide, the nitroso-derivative yields *ethyl α-nitro*-n-*valerate*, $CHEt\cdot CH(NO_2)\cdot CO_2Et$, as a yellow oil, with D_4^{18} 1·0551, n_D^{18} 1·4595, and has a very strong odour.

Ethyl α-nitrosohexoate (Abstr., 1909, i, 454) has n_D^{20} 1·4515, and when the corresponding nitro-derivative is treated with concentrated potassium hydroxide solution, yellow crystals of *potassium α-nitrohexoate*, $C_4H_9\cdot CH(NO_2)\cdot CO_2K$, are formed, together with the potassium salt of α-oximinohexoic acid.

α-Oximinohexoic acid, $C_4H_9\cdot C(:N\cdot OH)\cdot CO_2H$, crystallises from water in colourless needles, m. p. 132° (decomp.).

Pure ethyl α-nitrosopropionate, prepared from ethyl α-formylpropionate, has n_D^{18} 1·4295, and can be kept for two or three days. The best method for transforming it into the isomeric α-oximino-ester is shaking for a few minutes with very dilute sodium hydrogen carbonate solution and keeping for two to three hours.

Ethyl oximinonitrophenylacetate, $NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CO_2Et$, crystallises from alcohol in colourless, glistening needles, m. p. 195°. It yields sparingly soluble mercurous and silver derivatives, and gives a dirty reddish-brown colour with ferric chloride. The *benzoyl* derivative, $NO_2\cdot C_6H_4\cdot C(CO_2Et):NO\cdot COPh$, has m. p. 145°, and its *methyl ether* forms colourless needles, m. p. 151°.

It has not been found possible to isolate a nitroso-derivative from ethyl dibenzoylsuccinate by the action of nitrous gases, although benzoic acid is eliminated.

Ethyl α-benzoylpropionate reacts with nitrous gases, yielding ethyl α-oximinopropionate and the corresponding acid (Ebert, *loc. cit.*).

J. J. S.

Synthesis of β-Methyl-αβ-diethylhydracrylic Acid and its Properties. I. Matschurevitsch (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 891—899. Compare Abstr., 1909, i, 304).—*Ethyl β-methyl-αβ-diethylhydracrylate* [*ethyl β-hydroxy-β-methyl-α-ethylvalerate*],

$$OH\cdot CMeEt\cdot CHEt\cdot CO_2Et,$$

is best prepared by mixing methyl ethyl ketone with ethyl α-bromobutyrate dissolved in dry benzene, and pouring on to dry zinc previously treated with sulphuric acid. The whole is heated on the water-bath in a reflux apparatus for some hours, after which the product is treated with water, fractionated, and purified. It is a colourless, mobile liquid, b. p. 115·5—116°/25 mm., 214—219°/760 mm. (decomp.), D_4^{23} 0·96230, which with barium hydroxide yields the *acid*, $OH\cdot CMeEt\cdot CHEt\cdot CO_2H$, of which the *potassium*, *sodium*, *barium*, *silver*, and *copper* salts are described.

With sulphuric acid the acid is decomposed, thus:

$$OH\cdot CMeEt\cdot CHEt\cdot CO_2H = H_2O + CMeEt{:}CEt\cdot CO_2H$$

and $$OH\cdot CMeEt\cdot CHEt\cdot CO_2H = H_2O + CO_2 + OH\cdot CMeEt\cdot CH_2Et.$$

When the ester is treated with phosphoric oxide, *ethyl β-methyl-α-ethyl-Δ$^{\alpha}$-pentenoate*, $CMeEt{:}CEt\cdot CO_2Et$, b. p. about 188—190°, is formed, which when treated with potassium hydroxide yields β-methyl-α-ethyl-Δ$^{\alpha}$-pentenoic acid, $CMeEt{:}CEt\cdot CO_2H$, of which a *bromide* and the *potassium*, *silver*, *lead*, and *calcium* salts were prepared. Z. K.

The Unary Termolecular Pseudo-ternary System: Acetaldehyde, Paracetaldehyde, and Metacetaldehyde. Andreas Smits and H. L. de Leeuw (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 318—329).—Observations relating to the connexion between acet-

aldehyde, paracetaldehyde, and metacetaldehyde are discussed, and it is shown that the apparently contradictory results relating to the conditions under which these substances are formed and transformed into one another can be accounted for on the assumption of a ternary equilibrium represented by:

Acetaldehyde ⇄ Paracetaldehyde.

⇖ ⇗

Metacetaldehyde.

On account of the conversion of metacetaldehyde into the other two isodynamic forms, previous attempts to determine the triple point of metacetaldehyde have given erroneous results. By a method in which the substance, contained in closed thin-walled capillary tubes, was immersed in baths of different temperatures, the melting point of metacetaldehyde under its own vapour pressure was found to be 246·2°. This is much higher than the temperatures, 184° and 167°, obtained by Roozeboom and Hollman respectively. H. M. D.

The System Acetaldehyde–Alcohol. Andreas Smits and H. L. de Leeuw (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 329—339).—Experiments have been made to determine the nature of the additive compounds which are formed in mixtures of acetaldehyde and ethyl alcohol. Mixtures which had been kept at the ordinary temperature for about a year, or heated for several hours at 100°, gave no indication of the presence of water when tested with anhydrous copper sulphate. When acetaldehyde-alcohol mixtures are left in contact with copper sulphate for a long time, a blue colour appears, however, and this is supposed to be due to the catalytic influence of the copper salt on the formation of acetal. This accelerating effect affords a convenient method for the preparation of acetal.

The mixing of acetaldehyde and alcohol is attended by a large diminution in volume, and it is found that the density of an equimolar mixture has a maximum value (D_4^{18} 0·8719) which is very much greater than that of either of the components. The density data indicate therefore the formation of a compound $CH_3{\cdot}COH,C_2H_5{\cdot}OH$.

Measurements of the boiling points of various mixtures at different pressures, and of the composition of the vapour emitted by these mixtures, were also made. The curves obtained by plotting boiling points against the composition of the liquid also indicate the formation of the above compound, and a further compound containing a larger proportion of alcohol. Similar conclusions are drawn from the heats of mixing, a maximum heat effect being obtained for an equimolar mixture.

The data obtained in freezing-point measurements confirm these results, and indicate with certainty the formation of compounds, $CH_3{\cdot}COH,C_2H_5{\cdot}OH$ and $CH_3{\cdot}COH,2C_2H_5{\cdot}OH$, which are considerably dissociated at their respective melting points, −122° and −123°.

H. M. D.

Preparation of Keten from Acetone. Julius Schmidlin and Maximilian Bergmann (*Ber.*, 1910, **43**, 2821—2823. Compare Wilsmore, Trans., 1907, **91**, 1938).—Keten appears to be stable

at fairly high temperatures, and a 14% yield can be obtained by passing the vapour of acetone through a hard glass tube filled with porous earthenware and heated at 500—600°. The decomposition of acetone appears to take place in two stages: (1) at about 500—600°, $2CH_3{\cdot}CO{\cdot}CH_3 = 2CH_2{:}CO + 2CH_4$, and (2) at higher temperatures, $2CH_2{:}CO = 2CO + C_2H_4$. It is impossible to prevent part of the keten from decomposing even at the lower temperature.

It is highly probable that in the preparation of keten from acetic anhydride, acetone is the first product formed. J. J. S.

A New Sugar, Verbascose, from the Root of Mullein. Émile Bourquelot and Marc Bridel (*Compt. rend.*, 1910, 151, 760—762*).—A description of the detection and isolation of a new polysaccharide occurring in the roots of *Verbascum thapsus*. The sugar, for which the name *verbascose* is suggested, crystallises in minute, spherular aggregates of slender needles, m. p. 219—220°, on the Maquenne block; $[\alpha]_D$ +169·9°. It appears to be analogous to stachyose, since, on hydrolysis, dextrose, lævulose, and galactose are produced. Verbascose does not reduce Fehling's solution; on oxidation with nitric acid, it yields mucic acid.

Verbascum thapsus appears also to contain a glucoside, hydrolysable by emulsin. W. O. W.

Purification of Starch. Giovanni Malfitano and Mlle. A. N. Moschkoff (*Compt. rend.*, 1910, 151, 817—819. Compare this vol., i, 301).—Further experimental details are given for the preparation of starch free from electrolytes by the method previously described. Potato starch is the variety most amenable to this method of purification. The material so obtained contains less than 0·02% of ash. With hot water it gives a colloidal solution less viscous than an ordinary starch solution, but from which the substance is precipitated by dilution. W. O. W.

The Adsorption of Acids by Carbohydrates. Fred. Robinson (*Proc. Camb. Phil. Soc.*, 1910, 15, 548—558. Compare Fenton and Gostling, Trans., 1898, 73, 554).—The dry carbohydrate is covered with chloroform or carbon tetrachloride, a standard solution of dry hydrogen chloride or bromide in the same solvent is then added, and, after several hours, a known volume is withdrawn, shaken with water, and titrated with barium hydroxide.

Carbohydrates adsorb the acids rapidly, the results agreeing well with an exponential adsorption formula, but the relative order of adsorption is not related to the chemical nature of the carbohydrate. It is also independent of chemical action, as the adsorptive power of starch is the greatest, although starch yields the smallest quantity of chloromethylfurfuraldehyde. Lactose and dextrose have the lowest adsorptive power, lactose and maltose differing widely. Lævulose and sucrose become pink, and finally black, with hydrogen bromide. C. H. D.

Hydrocellulose. Carl G. Schwalbe (*Zeitsch. angew. Chem.*, 1910, 23, 2030—2031).—The conclusions of Jentgen (this vol., i, 654) are erroneous, as the cellulose used would retain a considerable quantity of

* and *J. Pharm. Chim.*, 1910, [vii], 2, 481—490.

water, so that the acid is diluted with water, and is not in the so-called molecular condition. C. H. D.

Nitrous Esters of Cellulose. Paul Nicolardot and Georges Chertier (*Compt. rend.*, 1910, **151**, 719—722).—Estimation of the nitrogen in nitrated cellulose by the Schlœsing method always gives a higher result than when the analysis is effected in the Lunge nitrometer. This appears to be due to the existence of nitrous esters, which undergo immediate decomposition when dissolved in sulphuric acid. Attempts to prepare such compounds by the action of oxides of nitrogen on cotton under various conditions were unsuccessful, oxidation usually taking place. By their action on viscose, however, in presence of acetic acid, a product was obtained containing 3% of nitrogen (Schlœsing) or 5% (Lunge). This was freed from nitrates by treatment with acetone, in which the nitrites are insoluble.

The nitrous esters of cellulose are somewhat unstable, grey substances, pulverulent when dry, but gelatinous when wet. They are insoluble in water and organic solvents; alkalis bring about hydrolysis, nitrites being formed. Hydrolysis is slowly effected by water at the ordinary temperature, and in contact with alcohols, decomposition occurs, the corresponding aldehyde or acid being produced. The deterioration of nitrated cotton is probably connected with the presence of these substances. W. O. W.

Ammonium and Oxonium Perchlorates. Relationship between Constitution and Behaviour towards Water. Karl A. Hofmann, R. Roth, K. Höbold, and A. Metzler (*Ber.*, 1910, **43**, 2624—2630. Compare this vol., i, 105, 168, 187, 370).—The solution of perchlorates in water is primarily due to the formation of hydrates; electrolytic dissociation and hydrolysis are secondary phenomena. Quaternary ammonium perchlorates are not so readily soluble in water as the perchlorates derived from primary, secondary, and tertiary amines. Diazonium perchlorates and the perchlorates of the magenta and methylene-blue series are also sparingly soluble.

Oxonium perchlorates of the type $R_2O,HClO_4$ are readily soluble, whereas tertiary perchlorates, $R_3O\cdot ClO_4$, are sparingly soluble.

These phenomena are attributed to subsidiary valencies of the acidic H atom, which can be used up in attaching water to the molecule of the acid or salt.

The following salts are described: *Trimethylammonium perchlorate*, $NHMe_3\cdot ClO_4$, doubly refracting prisms and pyramids; at 17°, 20 grams dissolve in 100 of water; *trimethylamineoxide perchlorate*, $NMe_3O,HClO_4$, hygroscopic cubes; *ethylenediamine perchlorate*, $C_2H_8N_2,2HClO_4$, compact prisms, soluble in its own weight of water at 17°; *tetramethylammonium perchlorate*, $NMe_4\cdot ClO_4$, tetragonal crystals, decomposing above 300°, solubility 0·341 at 12°, 1·008 at 19°, and 1·554 at 25°; *tetraethylammonium perchlorate*, solubility 2·392 at 17°, decomposes above 300°; *trimethylethylammonium perchlorate*, long, rectangular prisms, solubility 11·06 at 17° and 11·97 at 20°; *trimethylbromoethyl perchlorate*, $C_2H_4Br\cdot NMe_3\cdot ClO_4$, rectangular plates, m. p. about 200° (decomp.), solubility 3·59 at 19°; *choline perchlorate*, $OH\cdot C_2H_4\cdot NMe_3\cdot ClO_4$, glistening, rectangular plates from absolute

alcohol, solubility 0·89 at 20°; *neurine perchlorate*, $C_2H_3\cdot NMe_3\cdot ClO_4$, short prisms, solubility 5·764 at 0°, also soluble in 30% hydrogen peroxide; *betaine perchlorate*, $C_2H_3O_2\cdot NMe_3\cdot ClO_4$, doubly refractive plates, solubility 17·73 at 19°; *diphenyliodonium perchlorate*, $IPh_2\cdot ClO_4$, colourless, felted needles, solubility 0·624 at 19·6°. The perchlorates of malachite-green, crystal-violet, and methylene-blue are so sparingly soluble that the solubilities can be estimated by the colorimetric method only. The perchlorates of the corresponding leuco-bases are much more readily soluble. *Magenta tetraperchlorate*, $C_9H_{17}N_3,4HClO_4$, is a dark orange-coloured, crystalline powder, obtained by mixing the monoperchlorate with 60% perchloric acid solution and ether; it decomposes above 300° and is hydrolysed by water to the monoperchlorate. *p*-Phenylenediamine, *p*-phenylenedimethyldiamine, acetyl-*p*-phenylenediamine, and *m*-phenylenediamine, all yield sparingly soluble crystalline diazonium perchlorates, that derived from *p*-phenylenediamine being extremely explosive. The diazo-compounds from *o*-phenylenediamine and *o*- and *p*-aminophenol do not yield crystalline perchlorates.

The following alkaloid perchlorates are formed as precipitates when acetic acid solutions of the base are mixed with excess of 20% perchloric acid solution: Cinchonine perchlorate (2), prisms; *strychnine perchlorate* (1), long needles, solubility 0·22 at 15°; *brucine perchlorate* (1), rhombic plates, solubility in 2% perchloric acid solution 0·15 at 18°; *morphine perchlorate* (1), glistening needles, solubility in 4% acid 0·44 at 15°; *cocaine perchlorate* (1), long needles, solubility in 8% acid 0·26 at 6°. The numbers refer to the number of molecules of acid combined with one molecule of alkaloid. Quinine, quinidine, kairine, thalline, nicotine, piperidine, piperazine, and solanine are not precipitated by 20% perchloric acid.

Anisaldehyde perchlorate, $2OMe\cdot C_6H_4\cdot CHO,HClO_4$, crystallises from ethereal solution in colourless prisms or plates, which deliquesce in contact with the air. *Chrysoquinone perchlorate*, $C_{18}H_{10}O_2,HClO_4$, forms dark violet-coloured prisms, decomposing at about 190°. Anthranol, anthraquinone, diphenylene oxide, and phenyl ether do not yield perchlorates, but dibromophenyl ether and dibromodiphenyleneoxide yield sparingly soluble perchlorates (3 mols. of oxygen compound to 1 of acid) which are hydrolysed by water.

Xanthoxonium perchlorate, $C_{13}H_9O\cdot ClO_4$, prepared from an ethereal solution of xanthhydrol and 70% perchloric acid, forms intensely yellow crystals; these decompose at 235°, and are hydrolysed by water to xanthhydrol and perchloric acid, but are more stable than the crystals of xanthone perchlorate. The group $X\cdot O\leqslant$ is thus comparatively stable (compare Baeyer, this vol., i, 763). J. J. S.

Some Derivatives of Pentamethylenediamine and a New Convenient Synthesis of 2 Methylpyrrolidine from Piperidine. Julius von Braun (*Ber.*, 1910, 43, 2864—2879).—2-Methylpyrrolidine, which cannot be obtained from piperidine in the same way that 2-methyldihydroindole is prepared from tetrahydroquinoline, has been synthesised as follows: Benzoylpiperidine is converted by phosphorus

pentachloride into benzoyl-ε-chloroamylamine, and this, for practical purposes, is changed by excess of alcoholic sodium iodide into benzoyl-ε-iodoamylamine. The latter reacts rapidly with warm alcoholic 33% trimethylamine to form *ε-benzoylaminotrimethylamylammonium iodide*, $NHBz\cdot[CH_2]_5\cdot NMe_3I$, m. p. 189°. (The corresponding chloride is an oil which yields a *platinichloride*, m. p. 198°.) The iodide is converted in the usual manner into a solution of the hydroxide, which, after evaporation to dryness, yields by distillation in a vacuum a mixture of *benzoyldimethylpentamethylenediamine*, $NHBz\cdot[CH_2]_5\cdot NMe_2$, b. p. 220—225°/10 mm. (*picrate*, oily; methiodide, m. p. 189°, as above), and *pentenylbenzamide*, $CH_2{:}CH\cdot[CH_2]_3\cdot NHBz$, b. p. 195°/13 mm., which is easily separated, owing to the insolubility of the latter in dilute acids. The solution of the unsaturated compound in concentrated hydrochloric acid, after many hours at 70°, yields on cooling impure benzoyl-δ-chloroamylamine, which is converted by concentrated hydrochloric acid at 150—160° into *δ-chloroamylamine hydrochloride*; this forms a *platinichloride*, m. p. 192°, and is converted into 2-methylpyrrolidine by warming with alkalis. Since the m.p.'s of the platinichloride and of the aurichloride, 181—192° (decomp.) and 184° respectively, of the 2-methylpyrrolidine thus prepared do not agree with those, 206—207° (decomp.) and 158—161° respectively, of Tafel and Fenner's 2-methylpyrrolidine, the author's base has been converted by exhaustive methylation into the quaternary methiodide, the platinichloride of which, decomp. 255°, blackening at 240°, agrees exactly with the corresponding derivative of Tafel and Fenner's base.

Benzoyldimethylpentamethylenediamine can be readily prepared by heating aqueous dimethylamine (2 mols.) and benzoyl-ε-chloroamylamine on the water-bath. By hydrolysis with hydrochloric acid at 150° it yields as-*dimethylpentamethylenediamine*, $NMe_2\cdot[CH_2]_5\cdot NH_2$, b. p. 181—182° (*aurichloride*, m. p. 168°). *Benzoyldiethylpentamethylenediamine*, $NEt_2\cdot[CH_2]_5\cdot NHBz$, b. p. 232—234°/10 mm., similarly prepared from diethylamine, yields by hydrolysis as-*diethylpentamethylenediamine*, b. p. 87—88°/10 mm. [*platinichloride*, m. p. 215° (decomp.); *picrate*, m. p. 110°]. *Benzoyldiisobutylpentamethylenediamine*, $NHBz\cdot[CH_2]_5\cdot N(C_4H_9)_2$, b. p. 250°/10 mm. (decomp.), yields by hydrolysis as-*diisobutylpentamethylenediamine*, b. p. 126—127°/11 mm. (*platinichloride*, m. p. 212°). These three *as*-dialkylpentamethylenediamines are almost odourless, remain unchanged above 200°, are almost unaffected by air, and do not react with nitrous acid. This inactivity is attributed to steric causes, not to a concentration of the basic properties at the tertiary nitrogen atom to such an extent that the primary nitrogen atom no longer exerts basic functions. The latter explanation is rejected because as-*phenylmethylpentamethylenediamine*, $NH_2\cdot[CH_2]_5\cdot NPhMe$, b. p. 180°/16 mm. (prepared by hydrolysing the benzoyl derivative obtained from methylaniline and benzoyl-ε-iodoamylamine), in which the tertiary nitrogen atom probably has a weaker basic function than the primary, reacts with nitrous acid without the evolution of a gas (probably, therefore, a nitroso-group enters the phenyl nucleus), and also because o-γ-*dimethylaminopropylaniline*, $NMe_2\cdot[CH_2]_3\cdot C_6H_4\cdot NH_2$, b. p. 151°/15 mm. [*picrate*, m. p. 173—174°; *platinichloride*, m. p. 213° (decomp.)], in which the aromatic amino-

group is certainly weaker than the aliphatic dimethylamino-group, reacts with nitrous acid with evolution of nitrogen, forming a substance which is soluble in alkalis and is therefore probably *o*-γ-dimethylaminopropylphenol. *o*-γ-Dimethylaminopropylaniline is obtained by hydrolysing its benzoyl derivative, which is prepared from *o*-γ-chloropropylbenzanilide and dimethylamine.

Di-ε benzoylaminodimethylamyl ammonium iodide,

$$(NHBz\cdot[CH_2]_5)_2NMe_2I,$$

m. p. 162°, obtained as a by-product in the reaction between dimethylamine and benzoyl-ε-iodoamylamine, is converted by hydriodic acid at 160° into *di-ε-aminodimethylamylammonium iodide dihydriodide*, $(HI,NH_2\cdot[CH_2]_5)_2NMe_2I$, m. p. 210°; the corresponding *dihydrochloride*, $(HCl,NH_2\cdot[CH_2]_5)_2NMe_2Cl$, has m. p. 240°, and forms a *platinichloride*, m. p. 221°. The dihydriodide by exhaustive methylation yields the tris-quaternary *ammonium iodide*,

$$NMe_3I\cdot[CH_2]_5\cdot NMe_2I\cdot[CH_2]_5\cdot NMe_3I,$$

which does not melt at 300°; the corresponding tris-quaternary *chloride* is extremely hygroscopic, and forms a *platinichloride*, m. p. 260°, blackening at about 250°. C. S.

Cyclic Imines. IV. Constitution of Hexamethyleneimine and the Action of αζ-Di-iodohexane on Bases. Julius von Braun (*Ber.*, 1910, 43, 2853—2864).—The presence of a seven-membered heterocyclic ring in hexamethyleneimine, which is denied by Blaise and Houillon (Abstr., 1906, i, 692), is proved by distilling *benzoylhexamethyleneimine*, b. p. 206—208°/19 mm., with phosphorus pentachloride and boiling the portion of the distillate which is insoluble in water with an excess of alcoholic sodium phenoxide for ten hours, whereby αζ-diphenoxyhexane is obtained in 65% yield.

The reactions between αζ-di-iodohexane and methylamine, dimethylamine, aniline, and piperidine do not yield a trace of hexamethyleneimine derivatives, the products being derivatives of αζ-diaminohexane and of α-pipecoline, and substances of high molecular weight. Thus αζ di-iodohexane and aqueous methylamine (4 mols.) in the presence of a little alcohol, after two days at the ordinary temperature, yield 10% of 1-methyl-2-pipecoline (identified in the form of the methiodide, m. p. 255°, and the platinichloride, decomp. 222°, obtained therefrom), 13% of dimethyl-αζ-diaminohexane (*dibenzenesulphonyl* derivative, m. p. 182°; *picrate*, m. p. 137°), and about 70% of a mixture of substances of high molecular weight. When heated on the water-bath for many hours, αζ-di-iodohexane and aniline (3 to 4 mols.) yield, not phenylhexamethyleneimine or phenyl-α-pipecoline, but about 50% of *diphenyl-αζ-diaminohexane*, $NHPh\cdot[CH_2]_6\cdot NHPh$, m. p. 74°, which forms a *picrate*, m. p. 172°, a *dibenzoyl* derivative, m. p. 163°, and a *dinitroso*-compound, m. p. 69°. αζ-Di-iodohexane and dimethylamine yield dimethyl-2-pipecolinium iodide and *tetramethyl-αζ-diaminohexane*, $NMe_2\cdot[CH_2]_6\cdot NMe_2$, b. p. 103°/20 mm., which forms a *picrate*, m. p. 162°, and a *methiodide*, which does not melt at 270°. αζ-Di-iodohexane and piperidine in alcoholic solution on the water-bath yield about 50% of *αζ-di-1-piperidylhexane*,

$$C_5NH_{10}\cdot[CH_2]_6\cdot C_5NH_{10},$$

b. p. 198°/16 mm. (*picrate*, m. p. 208°, blackening at 195°; *platinichloride*, m. p. 230°; *methiodide*, m. p. 240°), together with a quaternary *iodide*, $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NI<\begin{matrix}CHMe\cdot CH_2\\CH_2\text{—}CH_2\end{matrix}>CH_2$, m. p. 263°, which is identical with the product obtained from 2-pipecoline and αε-di-iodopentane.

The preceding behaviour of di-iodohexane with primary and secondary bases proves that caution is necessary in assigning cyclic structures to substances produced in reactions in which the reagents employed would, apparently obviously, produce ring compounds.

C. S.

Detection of Choline. Trimethylamine. Max Kauffmann and Daniel Vorländer (*Ber.*, 1910, 43, 2735—2743).—Choline platinichloride is dimorphous; it separates from water in monoclinic anhydrous crystals, and from dilute alcohol in regular octahedra and cubes or combinations of these. The monoclinic salt is slightly deeper orange in colour; both have m. p. 215—240° with frothing. The monoclinic salt is doubly refractive. The conversion of one form into the other takes place on crystallisation from water or 50% alcohol respectively, and affords a certain test for the presence of choline. Choline may also be detected by distillation with potassium hydroxide, when trimethylamine is formed and recognised by its odour. When trimethylamine is smelt for any length of time, the odour becomes firstly like that of a monoamine, and subsequently like that of ammonia which persists. Many other substances show a similar "reversal of odour."

When choline chloride is heated with excess of benzenesulphonyl chloride, trimethylchloroethylammonium chloride, $NMe_3(C_2H_4Cl)Cl$, is formed. The platinichloride crystallises in octahedra, m. p. 251°; the *aurichloride* forms slender, yellow, doubly-refractive needles. This chloroethyl base takes a middle position between neurine and choline in its toxic qualities.

By the interaction of aqueous trimethylamine and benzenesulphonyl chloride, a quaternary ammonium salt is obtained. The *platinichloride*, $(SO_2Ph\cdot NMe_3)_2PtCl_6,4H_2O$ (?), crystallises in anisotropic, prismatic, or tabular forms, m. p. 209—223°. The *aurichloride* separates in microscopic, doubly-refractive needles, m. p. 196°, decomp. 246°. The *chloride* was obtained in needles; it gives a yellow precipitate with picric acid. E. F. A.

Derivatives of Amino-alcohols. Ernest Fourneau (*J. Pharm. Chim.*, 1910, [vii], 2, 337—344, 397—401. Compare this vol., i, 246). —The first paper deals with the esterification of these alcohols, and shows (1) that the salts of such esters are easily crystallisable, and are convenient for the identification of the alcohols; (2) that they are readily obtained by mixing solutions in benzene of the amino-alcohols and the necessary acid chloride or bromide, and (3) that this method of formation appears to be analogous with Einhorn's method of using pyridine to promote esterification of alcohols, an additive product of the type $CH_2R\cdot N(CO\cdot R)R_2Cl$ being formed in both cases, which on

warming yields the ester. Maire's observation that amino-alcohols containing two ethyl groups attached to the nitrogen atom behave abnormally, is confirmed (Abstr., 1908, i, 248), but an ester was obtained in this case by avoiding the use of any solvent. Such amino-alcohols, however, behave normally with cinnamoyl chloride. The esters of the amino-alcohols are liquid, distil without decomposition, are stable towards alkalis, are easily hydrolysed by mineral acids, and are much less basic than the amino-alcohols; they have little or no odour. Their halogen acid salts crystallise well as a rule, but may be hygroscopic. The second paper describes a series of amides obtained by the application of the Schotten-Baumann reaction to the amino-alcohols. In these conditions no esterification of the hydroxyl group occurs.

Dimethylaminotrimethylcarbinol hydrochloride furnishes a *benzoate*, m. p. 202°, crystallising with 1 mol. of alcohol, a *cinnamate*, m. p. 208°, and an *isovalerate*, m. p. 125°. Dimethylaminodimethylethylcarbinol gives a *benzoate*, b. p. 150°/13 mm., a *diethylcarbamate*,

$$NMe_2\cdot CH_2\cdot CMeEt\cdot O\cdot CO\cdot NEt_2,$$

b. p. 136°/41 mm. [the *hydrochloride* of which, m. p. 142° (decomp.), crystallises from acetone in hygroscopic needles, and yields an *aurichloride*, m. p. 98°, which forms orange-red needles, whilst the *hydrobromide*, m. p. 148°, is very soluble in alcohol and exhibits a marked sedative action], a *valerate*, b. p. 128°/23 mm. (yielding a *hydrochloride*, m. p. 151°, and a *hydrobromide*, m. p. 126°, both of which are anæsthetics), a *bromovalerate hydrochloride*, m. p. 158°, which is markedly anæsthetic, a *diethylacetate hydrobromide*, m. p. 169°, a *bromodiethylacetate hydrochloride*, m. p. 160°, a *hexoate*, b. p. 152° (under reduced pressure), a *bromohexoate hydrochloride*, m. p. 130°, a *bromoheptoate hydrochloride*, m. p. 128° (which is markedly anæsthetic), and a *bromolaurate hydrochloride*, m. p. 99°. The higher homologues beyond the hexoate show increasingly the characters of the acid group, and exhibit the properties of soaps. The *hydrochlorides* of the *benzoyl* derivatives of the following amino-alcohols: dimethylaminomethyldiethylcarbinol, dimethylaminodimethylpropylcarbinol, diethylaminodimethylethylcarbinol, and dimethylaminodimethyl*iso*amylcarbinol melt at 180°, 146°, 140°, and 142° respectively. The last of these gives a *platinichloride*, m. p. 178°, and the amino-alcohol also furnishes a *cinnamate hydrochloride*, m. p. 110°.

Aminodimethylethylcarbinol gives with bromovaleryl chloride an *amide*, $CHMe_2\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CMeEt\cdot OH$, m. p. 93°, forming brilliant octahedral crystals. Valeryl chloride yields with the same amino-alcohol an *amide*, m. p. 50—60°, b. p. 190°/32 mm., and with methylaminodimethylethylcarbinol and iminobisdimethylethylcarbinol, *amides*, having b. p. 163°/25 mm. and 210°/23 mm. respectively; the second substance crystallises in spangles, and has m. p. 152—153°. All these amides are sedative, and some of them hypnotic; they are less toxic than the corresponding esters described in the first paper.

Ethyl chlorocarbonate reacts in presence of sodium hydrogen carbonate with aminodimethylethylcarbinol to form the *urethane*, $OH\cdot CMeEt\cdot CH_2\cdot NH\cdot CO_2Et$, b. p. 151—152°/17 mm., whilst with

the same alcohol propyl chlorocarbonate furnishes the *propyl* ester, having b. p. 174—175°. These urethanes are hypnotic in action, but must be given in large doses, for example, 0·4 gram per kilo. of body weight in rabbits. They are toxic to rabbits in doses of 1·8 grams per kilo.

Aminodimethylethylcarbinol with potassium *iso*cyanate yields the substituted *carbamide*, $OH\cdot CMeEt\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, m. p. 150°, which is a powerful hypnotic; the corresponding *methylcarbamide*, similarly obtained, has m. p. 128°, and *carbamide bisdimethylethylcarbinol*, m. p. 90° (approx.). T. A. H.

Carnitine; Synthesis of γ-Trimethylamino-β-hydroxybutyric Acid. R. Engeland (*Ber.*, 1910, 43, 2705—2707).—Carnitine, present in meat extract, has been pronounced to be γ-trimethylamino-α-hydroxybutyric acid (Engeland, Abstr., 1909, i, 557). It is shown now to differ from γ-trimethylamino-β-hydroxybutyric acid, which is obtained synthetically by heating epichlorohydrin with anhydrous hydrogen cyanide to form chlorohydroxybutyronitrile; this, when heated with alcoholic trimethylamine in sealed tubes at 110°, or even in open vessels at 70—80°, is converted into the *chloride* of *γ-trimethylamino-β-hydroxybutyronitrile*. The *aurichloride* of this compound crystallises in reddish-yellow prisms, m. p. 124—125°. Hydrolysis of the nitrile requires ten hours' boiling with a mixture of aqueous and alcoholic hydrochloric acid. A by-product is a bimolecular anhydride-like product, of which the sparingly soluble *aurichloride*, $C_{14}H_{30}O_5N_2,2AuCl_4$, was analysed. The *aurichloride* of *γ-trimethylamino-β-hydroxybutyric acid* crystallises in reddish-yellow plates, m. p. 145°, decomp. at 225°. The *chloride* crystallises in needles, sparingly soluble in alcohol. When heated with alcohol containing hydrogen chloride, it is converted quantitatively into the *ethyl* ester, the *platinichloride* of which sinters at 200°, m. p. 210—212°. These derivatives are very different from those of carnitine.

E. F. A.

Syntheses of Hydroxybetaines. II. Synthesis of γ-Trimethyl-β-hydroxybutyrobetaine (*dl*-*iso*Carnitine). Adolf Rollett (*Zeitsch. physiol. Chem.*, 1910, 69, 60—65. Compare this vol., i, 658).—*Ethyl γ-trimethylamino-β-hydroxybutyrate chloride*, $NMe_3Cl\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CO_2Et$, is formed when Lespieau's ethyl γ-chloro-β-hydroxybutyrate (Abstr., 1899, i, 243, 790) is heated with an alcoholic solution of trimethylamine for six hours at 100°. The *platinichloride*, $C_{18}H_{40}O_6N_2PtCl_6$, crystallises from 90% alcohol in slender, pale yellow needles, which decompose at 233—234°. The *platinichloride* of the corresponding acid,

$$[NMe_3\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CO_2H]_2PtCl_6,$$

forms orange-coloured crystals, decomposing at 248°, and is isomeric with carnitine platinichloride (m. p. 214—218°).

A by-product obtained in the preparation of the ester is trimethylethylammonium chloride, which is deposited as the *platinichloride*, $(NMe_3Et)_2PtCl_6$, in the form of pale orange-coloured plates decomposing at 281—284°. The corresponding *aurichloride*, $NMe_3EtCl,AuCl_3$, forms characteristic needles, which are unchanged at 290°. J. J. S.

Action of Ammonia on Unsaturated Acids. II. George L. Stadnikoff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 885—890. Compare Abstr., 1909, i, 772).—In order to confirm the explanation already given for the formation of imino-acids by the action of aqueous ammonia on unsaturated acids, a mixture of crotonic and aminoacetic acids was heated in a sealed tube at 120—130° with sufficient aqueous ammonia to convert both acids into their ammonium salts. The products of the reaction were ethyl β-aminobutyrate and *diethyl-β-iminobutyrateacetate*, $CO_2Et\cdot CH_2\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2Et$, b. p. 144°/19 mm., D_4^{20} 1·0340, n_D^{20} 1·4370, a colourless, mobile liquid, soluble in alcohol and ether, and readily saponified into β-iminoacetic-butyric acid, $CO_2H\cdot CH_2\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2H$, m. p. 200° (decomp.). To avoid the formation of β-amino-acid, and thus make this a convenient general method for the preparation of imino-acids, the ammonium salts are substituted by the potassium salts of the amino- and unsaturated acids. To prove that glycine unites with crotonic acid in the β-position, propaldehyde and potassium cyanide were made to react with the hydrochloride of ethyl aminoacetate, when *α-iminoacetic-butyric acid*, $CO_2H\cdot CHEt\cdot NH\cdot CH_2\cdot CO_2H,H_2O$, was formed. It forms large, elongated prisms, m. p. 104—105°. The *hydrochloride* forms small crystals, decomposing at 175—177°.

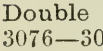
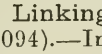
Thus, in the interaction of α-amino-acids with crotonic acid, αβ-imino-dialiphatic acids are formed. Z. K.

Synthesis of γ-Guanidinobutyric Acid. R. Engeland and Fr. Kutscher (*Ber.*, 1910, 43, 2882—2883).—This substance may be readily prepared by the following method. Concentrated solutions of cyanamide and of twice its weight of γ-aminobutyric acid are mixed, rendered alkaline with a few drops of ammonia, and kept for five weeks at the ordinary temperature, the evaporated ammonia being replaced from time to time. The guanidinobutyric acid which crystallises out is purified by conversion into the hydrochloride, which is sparingly soluble in concentrated hydrochloric acid and in alcohol. The *aurichloride*, $C_5H_{12}O_2N_3AuCl_4$, forms broad, lustrous plates, m. p. 198—200°. The *hydrochloride* regenerated from it has m. p. 184°; it is precipitated by phosphotungstic acid even from dilute solutions, but not by picric acid or sodium picrate. The synthetic acid is identical with that obtained by oxidation of arginine or agmatine.

R. V. S.

Action of Some Salts of Tervalent Metals on Thiocyanates. Corrado Bongiovanni (*Boll. chim. farm.*, 1910, 49, 789—791. Compare Abstr., 1908, i, 859).—Molybdenum thiocyanate is decolorised by the same substances which decolorise ferric thiocyanate. Chromic hydroxide and thiocyanic acid yield a reddish-violet solution, which is much less intensely coloured than that of ferric thiocyanate, and it behaves differently in other respects, for it is not hydrolysed appreciably, and is not decolorised by saline solutions, oxalic acid, or acetic acid. Vanadium thiocyanate behaves similarly to the ferric compound. The mode of formation and the properties of these substances do not accord with Tarugi's hypothesis (*loc. cit.*) as to their constitution. R. V. S.

Orientation in the Benzene Nucleus. JULIUS OBERMILLER (*J. pr. Chem.*, 1910, [ii], 82, 462—472).—A reply to, and a claim for priority over, Holleman. C. S.

Unsaturated Hydroaromatic Hydrocarbons with Semicyclic Double Linkings. KARL AUWERS and G. PETERS (*Ber.*, 1910, 43, 3076—3094).—In two papers published already (this vol., ii, 365, 367), Auwers and Eisenlöhr discuss the determination of constitution by optical methods, and point out the importance of ascertaining the normal value of the exaltation of refractivity and dispersivity in undisturbed conjugated systems and the influence thereon of various kinds of distortion. In pursuance of this object they are attempting to prepare and examine optically, substances derived from the three systems  ,  ·CH_3,  :CH_2, and the present paper gives the results of attempts to solve this question for the third of these

1 : 3-Dimethyl-Δ^3-*cyclo*hexen-5-one on treatment with magnesium methyl iodide furnishes 1 : 3 : 5-*trimethyl*-Δ^3-cyclo*hexen*-5-*ol*, m. p. 46°, b. p. 87—90°/17 mm., D_4^{20} 0·9132 to 0·9140, $n_D^{19·3}$ 1·47349, $n_\alpha^{19·3}$ 1·47053, and $n_\gamma^{19·3}$ 1·48715 (whence $\Sigma_\alpha = +0·36$, $\Sigma_D +0·34$, and $\Sigma_\gamma - \Sigma_\alpha + 9\%$); it is crystalline. On heating alone or with dehydrating agents, it yields a hydrocarbon having b. p. 63—64°/17 mm. or 151°/760 mm., D_4^{20} 0·821 to 0·828, n_α^{20} 1·467 to 1·477, n_D^{20} 1·471 to 1·481 (whence $\Sigma_\alpha = +0·68$ to $+1·02$, and $\Sigma_\gamma - \Sigma_\alpha$ varies from 24 to 40%). These data agree with the assumption that the hydrocarbon is 1 : 3-*dimethyl*-5-*methylene*-Δ^3-cyclo*hexene*, $CH_2<\begin{matrix}CMe=CH\\CHMe\cdot CH_2\end{matrix}>C:CH_2$, and belongs to the third system referred to above. On oxidation with permanganate, it furnishes a saturated neutral *substance*, $C_9H_{16}O_3$, m. p. 96—97°, but on treatment with ozone in acetic acid it yields γ-acetyl-β-methylbutyric acid (Knoevenagel and Brunswig, Abstr., 1902, i, 640), identical with that obtained by the action of permanganate or ozone on 1 : 3-dimethyl-Δ^3-*cyclo*hexen-5-one, which is probably formed as an intermediate product in the oxidation of the hydrocarbon. γ-Acetyl-β-methylbutyric acid has b. p. 140—142°/12 mm., $D_4^{18·7}$ 1·0614, $n_\alpha^{18·2}$ 1·44383, $n_D^{18·2}$ 1·44611, and yields a crystalline *semicarbazone*, m. p. 170—171°. The hydrocarbon on bromination and subsequent treatment with potassium hydroxide in alcohol yields mesitylene.

1 : 3-*Dimethyl*-5-*ethylidene*-Δ^3-cyclo*hexene*, b. p. 178°, D_4^{20} 0·833 to 0·837, n_α^{20} 1·476 to 1·483, n_D^{20} 1·480 to 1·487 (whence $\Sigma_\alpha = +0·80$ to $+1·05$, $\Sigma_D +0·84$ to $+1·10$, and $\Sigma_\gamma - \Sigma_\alpha = +27$ to 40%), probably identical with Klages' dihydroethylxylene (Abstr., 1907, i, 597), is obtained by heating the corresponding tertiary alcohol alone or with oxalic acid.

1 : 3-*Dimethyl*-5-iso*propylidene*-Δ^3-cyclo*hexene*, similarly prepared, has b. p. 101°/36 mm. or 196°/760 mm., D_4^{20} 0·841 to 0·848, n_α^{20} 1·481 to 1·492, n_D^{20} 1·485 to 1·496 (whence $\Sigma_\alpha = +0·70$ to $+1·20$, $\Sigma_D = +0·73$ to $+1·26$, and $\Sigma_\gamma - \Sigma_\alpha = 33$ to 51%). These hydrocarbons agree in general properties with the similar products containing semicyclic double linkings described by Wallach (Abstr., 1907, i, 425), but possibly all of them contained isomerides having two *end*ocyclic double linkings.

Pure hydrocarbons of this type probably have $\Sigma_\alpha = +1{\cdot}0$ to $1{\cdot}2$, $\Sigma_D = +1{\cdot}1$ to $1{\cdot}3$, and $\Sigma_\gamma - \Sigma_\alpha = 40$ to 50%. T. A. H.

Reducibility of Conjugated Double Linkings in Hydroaromatic Substances. Karl Auwers and G. Peters (*Ber.*, 1910, 43, 3111—3120).—An extension of the work described in the preceding abstract and this vol., i, 841. The results resemble those obtained by Klages (Abstr., 1904, i, 45, 1001) in the case of styrene derivatives, and show that the reducibility of the hydroaromatic hydrocarbons depends on the number, nature, and distribution of the side-chains attached to the carbon atoms in the double linkings of the conjugated system. This influence has been illustrated already by the reduction of 3-chloro-*iso*terpinolene to a mixture of menthenes (this vol., i, 122), by Semmler's reduction of chlorocarvenene to the corresponding hexadiene under similar conditions, and by the non-reducibility of hydrocarbons of this type, described by Rupe and Emmerich (Abstr., 1908, i, 556).

5-Chloro-1 : 3-dimethyl-$\Delta^{3:5}$-*cyclo*hexadiene, already prepared by Klages and Knoevenagel (Abstr., 1895, i, 654), has b. p. 68—70°/17 mm., $D_4^{15\cdot4}$ 1·0065, n_α 1·50022, n_D 1·50459 (whence $\Sigma_D = +0{\cdot}69$), but the sample was probably not quite pure. On careful reduction with sodium in wet ether it yielded 1 : 3-dimethyl-$\Delta^{3:5}$-*cyclo*hexadiene, b. p. 128—129°/760 mm., D_4^{20} 0·821, n_α^{20} 1·467, n_D^{20} 1·471 (whence $\Sigma_\alpha = +0{\cdot}62$, $\Sigma_D = +0{\cdot}68$, and $\Sigma_\gamma - \Sigma_\alpha = 26\%$), which furnished a *dihydrochloride*, b. p. 93—97°/16 mm., and is possibly identical with the dihydro-*m*-xylene described by Harries and Antoni (Abstr., 1903, i, 614), the difference in physical constants being perhaps due to impurity in both specimens. On further reduction in ether or, better, in alcohol, the chlorodimethyl*cyclo*hexadiene furnishes 1 : 3-dimethyl-Δ^4-*cyclo*hexene, b. p. 126—127°/760 mm., D_4^{20} 0·806, n_α^{20} 1·447, n_D^{20} 1·450 (whence $\Sigma_\alpha = +0{\cdot}26$, $\Sigma_D = +0{\cdot}24$, and $\Sigma_\gamma - \Sigma_\alpha = +9\%$) (compare Knoevenagel, Abstr., 1897, i, 606), which yields a *monohydrochloride*. T. A. H.

Derivatives of 1 : 3-Dichloro-4-iodobenzene with a Multivalent Iodine Atom. Conrad Willgerodt and Mathias Böllert (*Ber.*, 1910, 43, 2641—2646).—2 : 4-Dichloroaniline is best prepared by the action of concentrated hydrochloric acid and potassium chlorate on acetanilide and subsequent hydrolysis of the acetyl derivative by boiling with hydrochloric acid. A small amount of *s*-trichloroaniline is formed at the same time, but this is readily removed, as it is insoluble in hydrochloric acid. The dichloroaniline can be transformed into the corresponding 1 : 3-*dichloro*-4-*iodobenzene*, $C_6H_3Cl_2I$, by the Sandmeyer reaction. The iodo-derivative has b. p. 257° (corr.), and yields a *dichloride*, $C_6H_3Cl_2{\cdot}ICl_2$, in the form of pale yellow needles, which decompose at 107°. 1 : 3-*Dichloro*-4-*iodosobenzene*, $C_6H_3Cl_2{\cdot}IO$, is a yellow-coloured powder with the characteristic iodoso-odour, and decomposes at about 196°. It does not yield stable salts. The *chromate* forms a red powder. *Di* m-*dichlorophenyl-iodonium hydroxide*, $(C_6H_3Cl_2)_2I{\cdot}OH$, yields a faintly alkaline aqueous solution; the *iodide*, $(C_6H_3Cl)_2I{\cdot}I$, forms a yellow, crystalline precipitate, which decomposes at 135°; the *bromide* decomposes at 169°; the *chloride*, $(C_6H_3Cl_2)_2I{\cdot}Cl$,

is more readily soluble, and decomposes at 185°; the *platinichloride*, $C_{24}H_{12}Cl_{14}I_2Pt$, forms red needles, decomposing at 166°; the *mercurichloride*, $C_{12}H_6Cl_7IHg$, crystallises from alcohol in needles, m. p. 164° (decomp.), and the *dichromate*, $C_{24}H_{12}O_7Cl_8I_2Cr_2$, forms an orange-coloured precipitate, which is very unstable and explodes at 150°.

o-*Tolyl*-1 : 3-*dichlorophenyliodoniumiodide*, $C_6H_4Me\cdot I(C_6H_3Cl_2)\cdot I$, prepared by Meyer and Hartmann's method (Abstr., 1894, i, 242) by shaking equivalent quantities of *o*-iodotoluene and 1 : 3-dichloro-4-iodosobenzene with freshly precipitated silver oxide and water and reducing with sulphur dioxide, is yellow, and has m. p. 127°. The *hydroxide* is soluble in water, yielding a faintly alkaline solution; the *chloride*, $C_{13}H_{10}Cl_3I$, is colourless, and has m. p. 203°; the *bromide*, $C_{13}H_{10}Cl_2BrI$, crystallises from ether in plates, sinters at 170°, and decomposes at 185°; the *nitrate*, $C_{13}H_{10}O_3NCl_2I$, has m. p. 183° (decomp.); the *dichromate*, $C_{26}H_{20}O_7Cl_4I_2Cr_2$, is yellow, and decomposes at 141°; the *mercurichloride*, $C_{13}H_{10}Cl_5IHg$, forms colourless needles, m. p. 163°.

Phenyl-1 : 3-*dichlorophenyliodonium iodide*, $C_6H_3Cl_2\cdot IPh\cdot I$, is yellow, but turns red on exposure to the air, and has m. p. 133°; the *chloride*, $C_{12}H_8Cl_3I$, crystallises in colourless needles, m. p. 203°; the *bromide* crystallises from alcohol in plates, m. p. 196°; the *platinichloride*, $C_{24}H_{16}Cl_{10}I_2Pt$, forms yellow needles, m. p. 156° (decomp.), and the *dichromate*, $C_{24}H_{16}O_7Cl_4I_2Cr_2$, has m. p. 146° (decomp.).

1 : 3-*Dichlorophenyl*-1 : 3-*dichloro*-4-*iodophenyliodonium chloride*, $C_6H_3Cl_2\cdot I(C_6H_2Cl_2I)\cdot Cl$, crystallises from alcohol, and has m. p. 160°; the *bromide* crystallises in colourless needles, m. p. 131—132°; the *iodide*, $C_{12}H_5Cl_4I_3$, has m. p. 103°; the *dichromate*, $C_{24}H_{10}O_7Cl_8I_4Cr_2$, decomposes at 173°, and the *platinichloride*, $C_{24}H_{10}Cl_{14}I_4Pt$, forms a sparingly soluble, orange-coloured precipitate, m. p. 156°, after softening at 145°. J. J. S.

Limits of Activity of Chloromonoiodobenzenes with Regard to the Formation of Compounds with Multivalent Iodine. Conrad Willgerodt and Karl Wilcke (*Ber.*, 1910, **43**, 2746—2756). —s-*Trichlorophenyl iododichloride*, $C_6H_2Cl_3\cdot ICl_2$, crystallises in large, compact, sulphur-coloured leaflets, decomp. 100°.

s-*Trichloroiodosobenzene* is a slightly yellow, amorphous substance, which softens at 91°, decomp. 106°. The *basic sulphate*,

$$[C_6H_2Cl_3\cdot I(OH)]_2SO_4,$$

prepared by pouring 10% sulphuric acid on the iodoso-compound, is a colourless, crystalline powder, decomp. 168°. The *basic nitrate* is a bright yellow, crystalline mass, decomp. 143·4°, with evolution of red fumes. The *acetate* is obtained in colourless prisms grouped in rosettes, m. p. 166·8°.

s-Trichloroiodoxybenzene could not be obtained from the iodoso-compound.

Phenyl-s-*trichlorophenyliodinium chloride*, $C_6H_2Cl_3\cdot IPhCl$, is a yellow powder, m. p. 118—119°. The corresponding *iodide* begins to fuse at 90°, is melted clear at 140—150°, decomp. above 200°.

as-*Trichlorophenyl iododichloride* crystallises in small, sulphur coloured needles, decomp. 90°.

as-*Trichloroiodosobenzene* softens at 168°, decomp. 184°.

as-*Trichloroiodoxybenzene*, $C_6H_2Cl_3 \cdot IO_2$, prepared by oxidation of the iodide chloride with sodium hypochlorite, forms needles, decomp. 240° without explosion.

as-Tetrachloroaniline has m. p. 89°. *as*-Tetrachloroiodobenzene does not form an iododichloride, and parts with iodine when chlorinated. Pentachloroaniline has m. p. 232°. On diazotisation and addition of potassium iodide, pentachloroiodobenzene is obtained in colourless crystals, m. p. 208·5°; it does not give an iododichloride.

It would seem that no iodoxy-compound is formed when iodine is situated between two halogen atoms; apparently these exercise a neutralising influence on the valency of the iodine atom, and prevent the attachment of the second oxygen atom. E. F. A.

Action of Nitric Acid on Saturated Hydrocarbons. IV. S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 581—585. Compare Abstr., 1909, i, 372).—When saturated hydrocarbons are nitrated with nitric acid, it is found that with the diminution of the relative quantity of the latter, the nitration products increase, whilst the oxidation processes decrease. Now, aluminium nitrate, $Al(NO_3)_3,9H_2O$, melts at 73°, and decomposes completely into aluminium hydroxide and nitric acid at 140°, and between these two temperatures there is a certain equilibrium between the salt and its decomposition products. If, therefore, this salt is used for nitration, within these temperature limits the nitric acid will be used up as formed, and the equilibrium will thus be constantly disturbed. The acid will thus always be present in a relatively small quantity; the yield of nitration products should, therefore, be better than if an equivalent quantity of free nitric acid were employed. Experiments with *cyclo*hexane at 115—120° completely confirmed these considerations, a yield of 56·7% of mononitro-product being obtained; free nitric acid has never given such a high yield. *cyclo*Hexanone, possibly its nitro-derivative, $C_6H_{11}O_3N$, and *dinitrodicyclohexane*, $C_{12}H_{20}O_4N_2$, m. p. 216·5—217° (corr.), were formed as by-products. The latter, crystallising in small needles, was also obtained synthetically. Z. K.

*cyclo*Hexyl-*ψ*-nitrole. S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 585—586).—When a few pieces of ice and then dilute sulphuric acid are added to a mixture of an alkaline solution of nitro-*cyclo*hexane and sodium nitrite, a blue oil at once separates, and collects at the bottom of the vessel. After some time, the oil is gradually converted into colourless crystals, which rise to the top of the liquid. These two substances are regarded as two modifications of the *ψ*-nitrole, the blue liquid being unimolecular, the solid, bimolecular.

Solid *cyclohexyl-ψ-nitrole*, $C_6H_{10}O_3N_2$, m. p. 70—71° (decomp.), gives a blue solution in chloroform, and is oxidised by chromic acid in acetic acid solution, forming 1 : 1-*dinitrocyclohexane*, b. p. 142—143°/35 mm., D_4^{21} 1·2452, n_D^{21} 1·4732, a heavy, yellow oil with a fairly pleasant odour. Z. K.

Action of Nitric Acid on Methyl*cyclo*hexane. S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 691—701).—When methyl*cyclo*hexane is nitrated with nitric acid (D 1·2) or aluminium nitrate in a sealed tube, the chief product is the 1-nitro-derivative, the 3- and 4-nitro-derivatives also being obtained, more of the former when nitric acid is employed, and more of the latter with aluminium nitrate.

1-*Nitro*-1-*methyl*cyclo*hexane*, $C_7H_{13}O_2N$, b. p. 109—110°/40 mm., D_4^0 1·0547, D_4^{20} 1·0384, n_D^{20} 1·4580, is a colourless liquid with a pleasant odour; when heated with nitric acid, it is partly oxidised to succinic and oxalic acids, and with tin and hydrochloric acid it yields 1-amino-1-methyl*cyclo*hexane.

3-*Nitro*-1-*methyl*cyclo*hexane*, mixed with a very small quantity of the 1-nitro-derivative, has b. p. 119—120°/40 mm., D_4^0 1·0547, D_4^{19} 1·0382, n_{19} 1·4618, yields on reduction 3-*amino*-1-*methyl*cyclo*hexane*, b. p. 152—153°/752 mm., D_4^{19} 0·8562, n_D^{19} 1·4558, which is optically inactive, and gives a *benzoyl* derivative, m. p. 95—97°. As a by-product in the formation of the amine, 1-methyl*cyclo*hexan-2-one, $C_7H_{12}O$, is obtained; the latter compound is also formed by the oxidation of an alkaline solution of the nitro-compound with potassium permanganate, or by the action of sulphuric acid on the potassium nitro-compound. It has b. p. 168—169° (corr.), D_4^{17} 0·9179, n_D^{17} 1·4453, and yields two *semicarbazones*, m. p. 179—180° and 167—169°. When oxidised with permanganate, the nitro-compound yields α- and β-methyladipic acids.

Nitro*cyclo*hexane, b. p. 123—124°/40 mm., D_4^{18} 1·0459, n_D^{18} 1·4684, seems identical with the substance obtained by Zelinsky (Abstr., 1908, i, 864). When oxidised, it yields adipic acid. Besides nitro-compounds, nitric acid, when acting on methyl*cyclo*hexane, yields a number of oxidation products, namely, adipic, succinic, oxalic, glutaric, and pyrotartaric acids. The nature of the oxidation processes is discussed.

The nitro-compound from naphtha methyl*cyclo*hexane could not be obtained pure. The impure product has b. p. 109—110°/40 mm., D_4^{20} 1·0254, D_4^0 1·0430, n_D^{20} 1·4553. With tin and hydrochloric acid it gave an *amine*, b. p. 143—145°/755 mm., D_4^0 0·8632, D_4^{17} 0·8493, n_D^{17} 1·4509, the *benzoyl* derivative, $C_7H_{13}\cdot NH\cdot COPh$, of which has m. p. 99—100°. Z K.

Reduction of Nitro-derivatives by Spongy Copper. Alphonse Mailhe and Marcel Murat (*Bull. Soc. chim.*, 1910, [iv], 7, 952—956).—Bougault has observed (Abstr., 1909, ii, 310; compare Bach, this vol., ii, 31) that sodium hypophosphite added to copper sulphate solution furnishes a precipitate of spongy copper, which, in presence of sodium hypophosphite, decomposes water, liberating hydrogen. This process has been applied to the reduction of nitro-derivatives dissolved in alcohol, and gives good yields, complete in some cases, of the corresponding amines. The presence of halogen atoms or hydroxy-groups in the nitro-derivatives does not impede the reaction, and the halogen or hydroxy-group remains unattacked in the aromatic nucleus. The reaction is likely to be useful in the manu-

facture of aminophenols. Reduction is not effected when hydrogen under pressure is applied to a suspension of spongy copper in a solution of a reducible substance.

The substance to be reduced is dissolved in alcohol and placed in a flask with spongy copper. The flask is provided with a stopper carrying a reflux apparatus, and a bromine tube holding a supply of sodium hypophosphite solution, which is added from time to time as the action slackens. The nitro-derivatives tried include the following: nitroethane, *o*- and *p*-nitrotoluene, *o*-chloronitrobenzene, *p*-bromonitrobenzene, nitronaphthalene, *o*-nitrophenol, and 2 : 3-dinitrophenol.

T. A. H.

Spontaneous Decomposition of Phenylnitromethane. Otto Dimroth (*Ber.*, 1910, **43**, 2767—2768).—Crystals of dibenzhydroxamic acid, m. p. 161°, were obtained in quantity from phenylnitromethane preparations which had been kept for a long time. E. F. A.

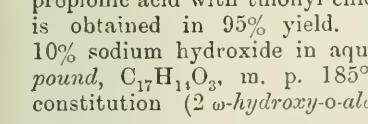
Some New Derivatives of Diphenylmethane. Luigi Mascarelli, B. Toschi, and T. Zambonini (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 338—342. Compare Mascarelli, this vol., i, 725).—*4 : 4′-Dichloro-2 : 2′-dinitrodiphenylmethane*, obtained by means of the Sandmeyer reaction from the corresponding diamino-derivative, forms slightly yellow, rhombic tablets, m. p. 121—122°. On reduction with tin and hydrochloric acid in alcoholic solution it yields *4 : 4′-dichloro-2 : 2′-diaminodiphenylmethane*, which crystallises in colourless needles, m. p. 130—131°. When diazotised and treated with potassium iodide, it is converted into *4 : 4′-dichloro-2 : 2′-di-iododiphenylmethane*, which forms colourless crystals, m. p. 77—78°.

2 : 2′-Di-iodo-4 : 4′-tetramethyldiaminodiphenylmethane,

$$NMe_2\cdot C_6H_3I\cdot CH_2\cdot C_6H_3I\cdot NMe_2,$$

can be obtained, but only in small amount, by diazotising the corresponding amino-compound and treating it with potassium iodide. It forms colourless scales, m. p. 123°. R. V. S.

Derivatives of *iso*Naphthafluoren (*o*-Phenylene-*ββ*-naphthylenemethane). Johannes Thiele and Alexis Wanscheidt (*Annalen*, 1910, **376**, 269—279).—A modification of Kipping's method of preparing α-hydrindone (Trans., 1894, **65**, 485) from *β*-phenylpropionyl chloride (which is best prepared by warming *β*-phenylpropionic acid with thionyl chloride) is described, whereby the ketone is obtained in 95% yield. It reacts with *o*-phthalaldehyde and 10% sodium hydroxide in aqueous alcohol to form an additive *compound*, $C_{17}H_{14}O_3$, m. p. 185° (decomp.), which receives the annexed constitution (*2 ω-hydroxy-o-aldehydobenzyl-1-hydrindone*) because it



reduces ammoniacal silver nitrate and is converted into *iso*naphthafluorenone (*o*-phenylene-*ββ*-naphthylene ketone) (Abstr., 1909, i, 929) by boiling methyl-alcoholic potassium hydroxide. A better method is described for the preparation of *iso*naphthafluorenone. It forms an *oxime*, m. p. 231°, and by reduction with sodium amalgam or with zinc and potassium hydroxide, is converted into *isonaphthafluorenol*,

$OH\cdot CH<^{C_6H_4}_{C_{10}H_6}$, m. p. 185°. This alcohol forms an *ether*, $O(C_{17}H_{11})_2$ (?), m. p. about 300°, an *acetate*, m. p. 97°, and in glacial acetic acid is converted by hydrogen chloride into the *chloride*, $C_{17}H_{11}Cl$, m. p. 150°, and by hydrogen bromide in glacial acetic acid into the *bromide*, $C_{17}H_{11}Br$, m. p. 162° (decomp.), which is reduced to *isonaphthafluoren*, $C_{17}H_{12}$, m. p. 208°, by zinc and acetic and hydrochloric acids. *Diisonaphthafluorenyl*, $^{C_{10}H_6}_{C_6H_4}>CH\cdot CH<^{C_{10}H_6}_{C_6H_4}$, m. p. 260—270° (decomp.), is obtained by heating *iso*naphthafluorenyl bromide and sodium iodide in acetone. *Bisphenylene-bis-ββ-naphthylenethylene*, $^{C_{10}H_6}_{C_6H_4}>C:C<^{C_{10}H_6}_{C_6H_4}$, m. p. 232°, obtained by the interaction 5*N*-methyl-alcoholic potassium hydroxide and *iso*naphthafluorenyl bromide in an excess of acetone, crystallises in dark red leaflets; it can also be prepared by heating *iso*naphthafluoren or di*iso*naphthafluorenyl with lead oxide at 300°, and is reduced to the latter by sodium amalgam and boiling amyl alcohol. C. S.

Dinaphthylmethane and Naphthafluorene. Julius Schmidlin and Max Huber (*Ber.*, 1910, **43**, 2824—2837).—The three dinaphthylmethanes which are theoretically possible are all known, but the constitution of only one has been determined with certainty, namely, di-β-naphthylmethane, m. p. 92°, prepared by reducing di-β-naphthyl ketone (Richter, Abstr., 1881, 281). It is now shown that the hydrocarbon obtained by Grabowski (Abstr., 1875, 455) by condensing naphthalene with methylal in the presence of sulphuric acid is di-α-naphthylmethane, since it can be prepared from di-α-naphthylcarbinol by converting the latter into di-α-naphthylacetic acid, and distilling the acid when carbon dioxide is eliminated. The hydrocarbon described by Claus and Ruppel (Abstr., 1890, 510) must therefore be αβ-dinaphthylmethane.

The constitutions of the isomeric dinaphthaxanthones have also been established. The three isomerides formed from β-naphthol must have the O-bridge in the β-position in both naphthalene rings. The compound with m. p. 149° (Claus and Ruppel, *loc. cit.*) yields αβ-dinaphthylmethane when reduced, and must therefore be *dinaphthylene-αβ-ketone-ββ-oxide*, $^{C_6H_4\text{—}C\cdot CO\cdot C:CH}_{CH:CH\cdot C\text{--}O\text{--}C:CH}>C_6H_4$. Bender's β-dinaphthaxanthone, m. p. 194° (Abstr., 1887, 37), must have the carbonyl group in the α-position with respect to one naphthalene ring (Kostanecki, Abstr., 1892, 1098), and since it is not identical with Claus and Ruppel's xanthone, the carbonyl group must be in the α-position with respect to the second naphthalene ring, and the compound is therefore *dinaphthylene-αα-ketone-ββ-oxide*,

$$\begin{matrix} C_6H_4\text{—}C\cdot CO\cdot C\text{—}C_6H_4 \\ CH:CH\cdot C\text{--}O\text{--}C\cdot CH:CH \end{matrix}$$

γ-Dinaphthaxanthone, m. p. 241° (Kostanecki, *loc. cit.*), must be *dinaphthylene-ββ-ketone-ββ-oxide*, $C_6H_4<^{CH:C\cdot CO\cdot C:CH}_{CH:C\text{--}O\text{--}C:CH}>C_6H_4$.

Di-α-naphthylacetic acid, $(C_{10}H_7)_2CH\cdot CO_2H$, obtained by converting di-α-naphthylcarbinol (Schmidlin and Massini, Abstr., 1909, i, 561) into the carbinyl chloride, and then condensing this with magnesium and carbon dioxide, has m. p. 223°, and when heated at 250—260° and then at 300° yields di-α-naphthylmethane, m. p. 105° (corr.). Grabowski's hydrocarbon has the same melting point, and in its preparation according to Grabowski's method appreciable amounts of a *compound*, $C_{40}H_{32}O$, are obtained.

β-Iodonaphthalene is prepared readily by a modification of Jacobson's method (Abstr., 1881, 736), and the magnesium β-naphthyl iodide reacts with a dry ethereal solution of ethyl formate, yielding a product which is decomposed by dilute acid, giving di-β-naphthylcarbinol, β-dinaphthafluorene, naphthalene, and another product.

ββ-Dinaphthafluorene, $\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}\!>\!CH_2$ is somewhat sparingly soluble in cold ether, but is more soluble than the carbinol in hot light petroleum. It crystallises in large, colourless, nacreous plates, m. p. 190·5° (corr.), and its solutions do not fluoresce. It is isomeric with Bamberger and Chattaway's picylenemethane (Abstr., 1895, i, 293), and when oxidised with an acetic acid solution of chromic anhydride yields *ββ-dinaphthafluorenone*, $\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}\!>\!CO$, which crystallises from ether in large, orange-coloured needles, m. p. 163—165° (corr.). The ketone dissolves in concentrated sulphuric acid, yielding deep blue-coloured solutions, which turn brown when kept. The isomeric *αα-dinaphthafluorenone*, prepared by oxidising αα-dinaphthafluorene (Schmidlin and Massini, *loc. cit.*), crystallises in minute, deep red-coloured needles, m. p. 255°, and dissolves in concentrated sulphuric acid to red solutions.

Di-β-naphthylcarbinol, $CH(C_{10}H_7)_2\cdot OH$, crystallises from light petroleum (b. p. 110—150°) in nodular masses, m. p. 91° (corr.), containing petroleum of crystallisation. The carbinol also forms a definite *compound* with hexane, $C_{21}H_{16}O,2C_6H_{14}$; this has m. p. 116·5° (corr.), and the hexane is removed when the crystals are heated at 150° under reduced pressure. The carbinol has not been obtained in a crystalline form free from hydrocarbon of crystallisation.

Di-β-naphthylchloromethane, $CH(C_{10}H_7)_2Cl$, obtained by the action of hydrogen chloride on a warm benzene solution of the carbinol, crystallises in colourless prisms, m. p. 167° (corr.). Its solution in concentrated sulphuric acid is colourless, but gradually assumes a violet coloration, due to the formation of the carbinol. It reacts with water or concentrated sulphuric acid less readily than the isomeric αα-compound does. *Di-β-naphthylacetic acid*, $CH(C_{10}H_7)_2\cdot CO_2H$, crystallises from glacial acetic acid in felted needles, m. p. 182—183° (corr.), and yields a sparingly soluble *sodium* salt. In the preparation of the acid an appreciable amount of *tetra-β-naphthylethane*,

$$CH(C_{10}H_7)_2\cdot CH(C_{10}H_7)_2,$$

is formed. It crystallises from benzene in small prisms, m. p. 273·5° (corr.).

Tetra-α-naphthylethane (Schmidlin and Massini, *loc. cit.*), when

oxidised with chromic anhydride, yields an *oxide*, $C_{42}H_{28}O$, in the form of orange-red crystals, m. p. 257°.

Attempts to prepare di-α-naphthylketen-quinoline were unsuccessful.

Attempts to prepare tri-β-naphthylcarbinol by the action of β-naphthoyl chloride on magnesium β-naphthyl bromide gave an appreciable amount of an impure hydrocarbon, probably tri-β-naphthylmethane, m. p. 178°. J. J. S.

Some Amide Derivatives of Thiocarboglycollic Acid. Bror Holmberg and B. Psilanderhielm (*J. pr. Chem.*, 1910, [ii], 82, 440—450. Compare this vol., i, 361).—In the production of rhodanins from dithiocarbamates and chloroacetamide (Miolati, Abstr., 1893, i, 405), the authors find that the amino-group of the acetic acid derivative is always eliminated by the ring closure, the thiocarbamyl group exhibiting remarkable stability. This conclusion is drawn from experiments on the behaviour of chloroacetamide and of chloroacetanilide on *N*-substituted dithiocarbamates; thus, chloroacetamide reacts easily with aqueous potassium phenyldithiocarbamate (prepared from aqueous potassium hydroxide, aniline, and carbon disulphide, a little *s*-diphenylthiocarbamide, which is formed, being removed by filtration) to form *N*-phenylrhodanin. Chloroacetanilide and aqueous ammonium dithiocarbamate give, according to the conditions of the experiment, either thiocarbamylthioglycollanilide (which is converted into rhodanine by hot dilute sulphuric acid) or a mixture of trithiocarbodiglycollanilide and thiodiglycollanilide; alcoholic chloroacetanilide and aqueous ammonium dithiocarbamate yield only thiodiglycollanilide. Chloroacetamide and aqueous potassium *o*-tolyldithiocarbamate yield *N*-*o*-tolylrhodanine.

Phenylmethylthiocarbamylthioglycollic acid, $CO_2H\cdot CH_2\cdot S\cdot CS\cdot NPhMe$, m. p. 197—198° (decomp.), is obtained by heating aqueous trithiocarbodiglycollic acid and methylaniline, or, much better, by treating aqueous potassium phenylmethyldithiocarbamate with aqueous sodium chloroacetate and acidifying after one day; it forms an *ethyl* ester, m. p. 77°. The *amide*, $NPhMe\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NH_2$, m. p. 141—141·5°, obtained from chloroacetamide and aqueous potassium phenylmethyldithiocarbamate, is converted into the free acid by hot dilute sulphuric acid, and into the ethyl ester by alcoholic sulphuric acid. The *anilide*, $NPhMe\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NHPh$, m. p. 139—139·5°, obtained from chloroacetanilide and potassium phenylmethyldithiocarbamate, is unchanged by hot dilute sulphuric acid, and is converted into the ethyl ester by alcoholic sulphuric acid.

Ethyl xanthoacetoanilide, $OEt\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NHPh$, m. p. 91·5—92°, obtained from chloroacetanilide and potassium xanthate in aqueous-alcoholic solution, and *ethyl trithiocarboglycollanilide*,

$$NHPh\cdot CO\cdot CH_2\cdot S\cdot CS_2Et,$$

m. p. 98°, obtained from chloroacetanilide and potassium ethyl trithiocarbonate, do not yield *N*-phenylrhodanine by elimination of alcohol and ethyl mercaptan respectively. C. S.

Isomerism in Compounds with Two Similar Asymmetric Nitrogen Atoms. Edgar Wedekind and Otto Wedekind (*Ber.*, 1910, 43, 2707—2719).—*Trimethylene*-bis-(*phenylmethylethylammonium*

iodide), $CH_2(CH_2{\cdot}NMeEtPhI)_2$, has been prepared in two ways: by the action of 2 mols. of methyl iodide on trimethylene-bis-ethylaniline, and by the addition of ethyl sulphate to trimethylene-bis-methylaniline, and interaction of the product with potassium iodide. In both cases the product obtained was a mixture of two isomeric iodides, a small quantity of a monomethiodide being also formed by the first method. The difference between the two iodides persists in their derivatives: those derived from the less fusible iodide are distinguished as *meso-*, those from the more fusible iodide as *para*-compounds. The meso-*iodide* has decomp. 222°, and crystallises in transparent prisms; the para-*iodide* forms opaque, prismatic aggregates (decomp. 177°). The meso-*platinichloride* forms monoclinic plates (decomp. 222°); the isomeride crystallises in monoclinic prisms, also m. p. 222°. The meso-*aurichloride* has decomp. 215°; the para-compound, decomp. 205—206°. The meso-*picrate* has m. p. 129°, forming indefinite crystals; the transparent prisms of the para-*picrate* show m. p. 165°. The meso-d-*camphorsulphonate* forms prismatic needles, m. p. 118—120°; the para-isomeride is very similar, m. p. 116—118°. The meso-d-*bromocamphorsulphonate* is crystalline, m. p. 163°; the isomeride is amorphous.

It has not been possible to transform salts of one series into the other.

Fractional crystallisation of the camphorsulphonates and bromocamphorsulphonates did not resolve either base into optically active forms.

Trimethylene-bis-ethylaniline (compare Fröhlich, Abstr., 1907, i, 346) has b. p. 240—242°/20 mm.

Trimethylene-bis-(phenyldimethylammonium iodide) crystallises in needles (decomp. 216°). E. F. A.

Electrolytic Reduction of Aromatic Sulphonyl Chlorides. Fritz Fichter and Walter Tamm (*Ber.*, 1910, 43, 3032—3038. Compare this vol., i, 20).—Suspensions of various aromatic sulphonyl chlorides in alcoholic sulphuric acid were reduced at a rotating lead cathode in a divided cell, the temperature being kept down by using a coiled lead tube, through which cold water flowed, as the anode. The most favourable current density varies from 0·04—0·07 ampere per sq. cm.; a further increase in the current density simply leads to the evolution of hydrogen. A copper cathode gives practically the same yield as one of lead, but with cathodes of silver, iron, zinc, nickel, or platinum the yield decreases in the order mentioned. Usually about one and a-half times the theoretical current was passed, the resulting product being a mixture of the disulphide, mercaptan, and sulphinic acid. To isolate these the reaction mixture was made alkaline with ammonia and the mercaptan oxidised by a current of air. After collecting the disulphide, sodium nitrite was added to the filtrate, and, after acidification with dilute sulphuric acid, a precipitate of the diarylsulphonylhydroxylamine derived from the sulphinic acid was obtained. These compounds are generally readily soluble in alkalis or alcohol, but sparingly so in benzene or ether.

α-Naphthalenesulphonyl chloride gave a yield of 81·3% of α-naphthyl disulphide and 13·6% of α-naphthalenesulphinic acid. The *di-α-naphthyl-*

sulphonylhydroxylamine, $(C_{10}H_7\cdot SO_2)_2N\cdot OH$, forms crystals, which have m. p. 120—130° (decomp.). The solutions decompose on warming into tri-α-naphthylsulphonamide. β-Naphthalenesulphonyl chloride gave an 80% yield of the β-naphthyl disulphide and 12·6% yield of β-naphthalenesulphinic acid. *Di-β-naphthylsulphonylhydroxylamine* separated as almost colourless crystals from dilute alcohol; it decomposes at 134°. From benzene-1 : 3-disulphonyl chloride, dithioresorcin was isolated by extracting the weakly acid solution with ether; yield 20—25%. The yield of benzene-1 : 3-disulphinic acid was 50%. Molecular-weight determinations in acetone of the corresponding disulphonylhydroxylamine showed it to be *bis*-m-*phenylenedisulphonylhydroxylamine*, $C_6H_4<^{SO_2\cdot N(OH)\cdot SO_2}_{SO_2\cdot N(OH)\cdot SO_2}>C_6H_4$; colourless crystals, decomposing at 212°.

p-Anisolesulphonyl chloride gave a 25·7—37% yield of p-methoxyphenyl disulphide. *Di*-p-*methoxybenzenesulphonylhydroxylamine* forms white needles, m. p. 120° (decomp.). *m*-Nitrobenzenesulphonyl chloride gave a 65—70% yield of *m*-aminophenyl disulphide sulphate.

The reaction mixture resulting from the interaction of sodium dimethylanilinesulphonate and phosphorus pentachloride was shown to contain the sulphonyl chloride by the preparation from it of p-*dimethylanilinesulphonanilide*, $NMe_2\cdot C_6H_4\cdot SO_2\cdot NHPh$; colourless crystals from alcohol, m. p. 176°. The crude reaction mixture containing the sulphonyl chloride gave *dithiodimethylaniline*, $S_2(C_6H_4\cdot NMe_2)_2$, on electrolytic reduction; m. p. 118°. The yield is very small because of the instability of the sulphonyl chloride. T. S. P.

Theory of Organic Reactions. Molecular Compounds as Preliminary Products in Cases of Condensation. I. Julius Schmidlin and Rudolf Lang (*Ber.*, 1910, 43, 2806—2820. Compare Uroczynski and Guye, this vol., ii, 699).—The authors accept Fittig's view that chemical reactions are preceded by the formation of more or less unstable additive compounds (compare Michael, Abstr., 1888, 1055; 1900, i, 321; 1904, ii, 64), and attention is drawn to the fact that in the case of triphenylmethyl derivatives and nitrosodimethylaniline chemical reactivity is accompanied by capacity for formation of additive compounds.

The examples investigated have been those of condensations which take place readily in the presence of a condensing reagent without the application of heat. In such cases the question is not complicated to any appreciable extent by the formation of additive compounds between the reacting substances and the condensing agent. The following pairs of substances have been examined: phenol and acetone, resorcinol and acetone, quinol and acetone, catechol and acetone, pyrogallol and acetone, and phenol and *cyclo*hexanone. In those cases in which condensation takes place with great readiness, it is found that additive compounds are formed, and that the relative amounts of the components in the additive compound are the same as the relative proportions in which they react to form the condensation product. Catechol and acetone, and also quinol and acetone, condense but slowly in the presence of concentrated hydrochloric acid and the additive compounds,

and condensation products bear no simple relationship to one another. In the latter case, the question is complicated by the formation of a definite *compound* of quinol with hydrogen chloride,

$$3C_6H_4(OH)_2,HCl.$$

Similarly, the additive compounds and condensation products of pyrogallol and acetone, and of phenol and *cyclo*hexanone, do not correspond.

In some cases the additive compounds have been actually isolated, and in all cases have been detected by melting-point curves.

Phenol and acetone yield the *compound*, $2Ph\cdot OH,COMe_2$, in the form of long needles, m. p. 15°, and the condensation product, di-*β*-*p*-hydroxyphenylpropane, $CMe_2(C_6H_4\cdot OH)_2$ (compare Dianin, Abstr., 1893, i, 214; Zincke and Grüters, *ibid*, 1906, i, 172), which is formed most readily when cold concentrated sulphuric acid is used as condensing agent. When crystallised from benzene, it retains benzene of crystallisation, $3C_{15}H_{16}O_2,C_6H_6$, which it loses when heated at 80° under reduced pressure.

Resorcinol and acetone yield the *compound*, $C_6H_4(OH)_2,2COMe_2$, m. p. 28°, which is comparatively stable. In determining melting points of mixtures of the two compounds, it is essential to avoid the entrance of traces of moisture, as such traces cause the mixtures to set to solid vitreous masses. The condensation product has not the composition stated by Causse (Abstr., 1892, 1312), but is to be represented as $C_{12}H_{14}O_2$. $C_6H_4(OH)_2 + 2CO(CH_3)_2 = C_{12}H_{14}O_2 + 2H_2O$, and has m. p. 230—240°.

Catechol and acetone yield a somewhat unstable *compound*,

$$C_6H_4(OH)_2,COMe_2,$$

m. p. −30°. The *condensation product* has the formula $C_{15}H_{14}O_4$, is formed in only small quantities, and decomposes at 270°. Quinol and acetone yield the *compound*, $C_6H_4(OH),COMe_2$, when sealed tubes are used (compare Habermann, Abstr., 1885, 53). Pyrogallol and acetone yield the *compound*, $C_6H_3(OH)_3,3COMe_2$, m. p. −24°. The *condensation product* contains C = 68·4 and H = 6·3%.

The *compound* of phenol and *cyclo*hexanone, $PhOH,C_6H_8O$, has m. p. −23°, and the condensation product, 1 : 1-*di*-p-*hydroxyphenyl*cyclo*hexane*, $C_6H_{10}(C_6H_4\cdot OH)_2$, obtained by using concentrated sulphuric acid, crystallises in colourless, rhombic plates containing alcohol, m. p. 186° (corr.).

α-Naphthol and *cyclo*hexanone react with concentrated sulphuric acid, yielding a *product*, $C_{26}H_{22}O$, m. p. 232°. This appears to be the anhydride of di-α-hydroxynaphthyl*cyclo*hexane, $C_6H_{10}<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O$, and is insoluble in alkalis. J. J. S.

An Easy Transformation of Asaryl Aldehyde into a Triphenylmethane Derivative. Rudolf Fabinyi and Tibor Széki (*Ber.*, 1910, 43, 2676—2684).—A good yield of *nonamethoxytriphenylmethane*, $CH[C_6H_2(OMe)_3]_3$, is obtained when asaryl aldehyde is heated with 25% hydrochloric acid for three hours on a water-bath. It may be freed from a brown, amorphous by-product by treatment with very dilute alkali hydroxide, and separates from alcohol in

colourless crystals, m. p. 184·5°. Its solution in sulphuric acid has a brilliant blue colour, and the crystals tend to turn yellow when kept in a calcium chloride desiccator. Concentrated nitric acid reacts with a glacial acetic acid solution of the nonamethoxy-derivative, yielding 4-nitro-1 : 2 : 5-trimethoxybenzene (Abstr., 1907, i, 45). Bromine reacts with a cold benzene solution of the nonamethoxytriphenylmethane according to the equation :

$$CH[C_6H_2(OMe)_3]_3 + 2Br_2 = C_6H_2Br(OMe)_3 + C_{19}H_{23}O_6Br_3.$$

The 4-*bromo*-1 : 2 : 5-*trimethoxybenzene* crystallises from alcohol in colourless, monoclinic prisms [$a : b = 0{\cdot}97506 : 1$; $\beta = 50°56'$], m. p. 54·5°. The same compound can be prepared more readily by the action of bromine on asaronic acid, or by the bromination of hydroxyquinol trimethyl ether. In the latter case, when an excess of bromine is used, dark blue, glistening crystals, $C_9H_{11}O_3Br_2$, are formed, but these are extremely unstable, and with water yield the bromotrimethoxybenzene. The second product, obtained by the action of bromine on the nonamethoxy-derivative, crystallises from benzene in slender prisms with a dark purple-blue colour, and is represented as a *bromine* additive compound of *hexamethoxydiphenylmethane*, namely,

$$BrMeO{:}C\langle\begin{matrix}C(OMe){:}CH\\CH{:}C(OMe)\end{matrix}\rangle C{:}CH{\cdot}CBr\langle\begin{matrix}C(OMe){:}CH\\CH{:}C(OMe)\end{matrix}\rangle C{:}OMeBr.$$

This formula is supported by the fact that the compound reacts with water, yielding asarylaldehyde and bromotrimethoxybenzene, $C_{19}H_{23}O_6Br_3 + H_2O = CHO{\cdot}C_6H_2(OMe)_3 + C_6H_2Br(OMe)_3$.

Dibromotrimethoxybenzene, $C_6HBr_2(OMe)_3$, prepared by the action of bromine on the monobromo-derivative, crystallises from benzene in long, colourless needles, m. p. 61°. 2 : 4 : 5 : 2′ : 4′ : 5′-*Hexamethoxydiphenyl*, $C_{12}H_4(OMe)_6$, can be obtained from the bromotrimethoxybenzene and copper at 270°. It crystallises from alcohol, has m. p. 180°, and yields a greenish-blue, unstable, additive compound with benzene.

2 : 4 : 5 : 2′ : 4′ : 5′-*Hexamethoxydiphenylacetonitrile*,

$$CN{\cdot}CH[C_6H_2(OMe)_3]_2,$$

is formed by the action of silver cyanide on the bromine additive compound of hexamethoxydiphenylmethane : $C_{19}H_{23}O_6Br_3 + 3AgCN = CN{\cdot}CH[C_6H_2(OMe)_3]_2 + 3AgBr + C_2N_2$, and crystallises from alcohol in slender needles, m. p. 155°.

Hydrogen chloride yields a deep blue additive compound with the nonamethoxytriphenylmethane, and when this is decomposed with water a colourless compound, m. p. 115—116°, is formed. J. J. S.

*cyclo*Butylcarbinol (ω-Hydroxymethyl*cyclo*butane) and its Isomerisation Under the Influence of Acids into Pentane Derivatives. Nicolaus J. Demjanoff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 837—855. Compare Abstr., 1903, i, 403 ; Perkin, Trans., 1901, 79, 329).—The most convenient method of obtaining *cyclo*butylcarbinol, $C_4H_7{\cdot}CH_2{\cdot}OH$, is by the reduction of ethyl *cyclo*butanecarboxylate with metallic sodium in alcoholic solution. When pure, it has b. p. 140—142·5°/750 mm., D_{10}^{10} 0·9199, D_{20}^{20} 0·9129, n_D^{20} 1·4449. When oxidised with chromic anhydride and sulphuric acid, it forms an *aldehyde*, of which the *sodium bisulphite* compound and a *semi-*

carbazone, m. p. 115—120°, were prepared in an impure state, and cyclo*butylcarbinyl* cyclo*butanecarboxylate*,

$$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CO_2\cdot CH_2\cdot CH<\begin{matrix}CH_2\\CH_2\end{matrix}>CH_2,$$

b. p. 218—220°, D_{19}^{19} 0·9795, n_D^{19} 1·4546, n_D^{21} 1·4533.

When heated with hydrogen bromide in a sealed tube at 100°, *cyclo*butylcarbinol is converted into *bromocyclopentane*,

$$\begin{matrix}CH_2\cdot CH_2\\|\\CH_2\cdot CH_2\end{matrix}>CHBr,$$

b. p. 137—139°, D_{19}^{19} 1·385, n_D^{19} 1·4875, which by means of zinc palladium and hydrobromic acid is reduced to *cyclo*pentane, b. p. 49—50°/750 mm., $D_{18\cdot5}^{18\cdot5}$ 0·7525, $D_{20\cdot5}^{20\cdot5}$ 0·7513, $n_D^{18\cdot5}$ 1·4087, $n_D^{20\cdot5}$ 1·4072.

Iodocyclopentane, $\begin{matrix}CH_2\cdot CH_2\\|\\CH_2\cdot CH_2\end{matrix}>CHI$, prepared similarly, is a colourless liquid, which turns green or brown when kept, has b. p. 162—164°/750 mm. (decomp.), D_4^0 1·7154, $D_4^{21\cdot5}$ 1·6825, n_D^{22} 1·5374, and with silver nitrate yields a secondary and a primary nitro-compound, which, without being isolated, were converted into the *ψ*-nitrole, $NO\cdot C_5H_8\cdot NO_2$, m. p. 96°.

With oxalic acid, *cyclo*butylcarbinol yields a hydrocarbon, b. p. 43·5—44°/755 mm., seemingly identical in physical properties with that obtained from *ω*-aminomethyl*cyclo*butane, and probably consisting of a mixture of *cyclo*pentene, $\begin{matrix}CH_2-CH\\|\\CH_2\cdot CH_2\end{matrix}>CH$, and a dicyclo*pentene*, $\begin{matrix}CH_2\cdot CH\\|\quad|\\CH_2\cdot CH\end{matrix}>CH_2$, or of the latter only.

The unsaturated hydrocarbon gives a *dibromide*, b. p. 192—195°, and with sulphuric acid an *alcohol*, b. p. 137—138°/753 mm., which with chromic anhydride and sulphuric acid yields *cyclo*pentanone, b. p. 130—131·5°, from which the oxime, m. p. 57°, and dibenzyl derivative, m. p. 189°, were prepared. The constitution of the unsaturated hydrocarbon and the isomerisation of *cyclo*butanes into *cyclo*pentanes is discussed. Z. K.

The Fluorene Series. A Correction. Julius Schmidt (*Ber.*, 1910, **43**, 2778—2779).—The substance described as fluorene ether by Schmidt and Stützel (this vol., i, 29) is, as Kliegl (this vol., i, 733) has in the meantime shown, a mixture of red dibiphenylene-ethylene and colourless diphenylenephenanthrone. E. F. A.

9-Formylfluorene or Diphenyleneacetaldehyde [Fluorene-9-aldehyde]. II. Wilhelm Wislicenus and Karl Russ (*Ber.*, 1910, **43**, 2719—2734. Compare Abstr., 1909, i, 241).—In the pure state only the crystalline *β*-form and the polymeride of double molecular weight exist; the oily *α*-form is in reality the *β*-form hindered from crystallisation by impurities. Formylfluorene tends to polymerise when distilled; the vapour is unimolecular, but it polymerises during cooling. The enolic form is unstable, and no ferric chloride coloration is

produced. The enolic potassium compound gives no coloration, but a precipitate of ferric hydroxide.

The *sodium bisulphite* compound crystallises in colourless, flat needles, m. p. 151—152° (decomp.). The *O*-acetate crystallises in platelets, m. p. 132—133°, and forms a *dibromide*,

$$\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>\!CBr\cdot CHBr\cdot OAc,$$

separating in colourless plates, m. p. 146—147° (decomp.). By the action of dry ammonia, a colourless compound, m. p. 148—149°, is formed, either *iminomethylfluorene*, $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>\!CH\cdot CH{:}NH$, or *amino-methylenefluorene*, $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>\!C{:}CH\cdot NH_2$. When heated above the melting point, a yellow compound is formed, which crystallises from nitrobenzene in small, golden-yellow prisms, m. p. 316—317°.

This dissolves in alcoholic potassium hydroxide or sodium ethoxide with a bluish-red coloration, which slowly disappears on standing; this colour change is attributed to conversion into the desmotropic form.

Formylfluorenemonoethylanilide, $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>\!C{:}CH\cdot NEtPh$, prepared by interaction of the components, crystallises in slender, canary-yellow prisms, m. p. 95—96°. The corresponding *piperidine* derivative, prepared in alcoholic solution, crystallises in yellow plates.

Formylfluorene-α-oxime, $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>\!CH\cdot CH{:}N(OH)$, probably the *anti*-form, crystallises in colourless needles, m. p. 132—133°, colouring at 166°. The *β-oxime*, probably the *syn*-form, crystallises in similar needles, m. p. 166—167°.

9-*Cyanofluorene* [*fluorene-9-carboxylonitrile*], $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>\!CH\cdot CN$, produced by the action of thionyl chloride on the oxime, forms long, lustrous, colourless needles, m. p. 151—152°. It dissolves in warm sodium hydroxide with a yellow colour and bluish-green fluorescence.

Formylfluorenebenzoylhydrazide separates in lustrous, light yellow needles, m. p. 233—234°. On evaporation of solutions of the phenylhydrazone, an oxidation product, m. p. 155—156°, is formed, probably an *azo*-compound. This reacts with bromine, forming a p-*bromobenzeneazomethylenefluorene dibromide*, $C_{20}H_{13}N_2Br_3$, crystallising in dark red needles, m. p. 210—211°. It is more easily obtained from *formylfluorene*-p-*bromophenylhydrazone*, which crystallises in lustrous, yellow plates, m. p. 158—159° (decomp.), and yields p-*bromobenzeneazomethylenefluorene*, $C_{13}H_8{:}CH\cdot N{:}N\cdot C_6H_4Br$, on oxidation, crystallising in lustrous, deep red needles with a blue reflex, m. p. 187—188°, and dissolving in concentrated sulphuric acid with an intense violet coloration.

Formylfluorenehydrazone forms colourless, lustrous, silky needles, m. p. 158—160°; it readily undergoes oxidation to *azomethylene fluorene*, $C_{13}H_8{:}CH\cdot N{:}N\cdot CH\cdot C_{13}H_8$, crystallising in very dark red, lustrous prisms, with a blue reflex, m. p. 290° (about).

Formylfluorenecyanohydrin forms colourless, slender, silky needles,

m. p. 142—143°. When heated with concentrated hydrochloric acid in sealed tubes at 125°, *fluorene-9-glycollic acid*, $C_{13}H_9\cdot CH(OH)\cdot CO_2H$, is formed in colourless plates, m. p. 194—195°. When boiled with potassium ethoxide, *cyanomethylenefluorene*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C\!:\!CH\cdot CN$, is obtained as a yellow, crystalline substance, m. p. 109—110°. It is remarkably stable towards hydrolysing agents.

By the action of bromine on formylfluorene an oil is produced. When dissolved in alcohol, the *acetal*, $C_{18}H_{19}O_2Br$, crystallises in colourless needles, m. p. 119—120°.

Di-biphenylenesuccinaldehyde, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C(CHO)\cdot C(CHO)\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$, is obtained on oxidising formylfluorene with ferric chloride in acetic acid solution; it crystallises in colourless, lustrous prisms, m. p 215—216°. Potassium ethoxide converts it into potassium formate and dibiphenylene-ethane. E. F. A.

Formation of an Ethylene Oxide from the Quaternary Base of Phenylmethylhydroxyethylamine. Paul Rabe and Julius Hallensleben (*Ber.*, 1910, **43**, 2622—2623. Compare this vol., i, 317).—It is shown that α-phenylpropylene αβ-oxide is formed when the aqueous solution of Emde and Runne's (this vol., i, 479) base from the methiodide of α-amino-α-phenyl*iso*propyl alcohol is heated.

The *oxide*, $\begin{matrix}CHPh\\CHMe\end{matrix}\!>\!O$ (yield 40%), is a colourless liquid, b. p. 200°/752 mm., is heavier than water, and has a characteristic odour. J. J. S.

Unsaturated Hydroaromatic Acids with One Semicyclic Double Linking, and Their Derivatives. Karl Auwers and G. Peters (*Ber.*, 1910, **43**, 3094—3110. Compare this vol., i, 826, 827).—When 1 : 3-dimethyl-Δ^3-*cyclo*hexen-5-one is condensed with ethyl bromoacetate in presence of zinc and benzene, the product obtained is *ethyl* 1 : 3-*dimethyl*-Δ^3-cyclo*hexene*-5-*ol*-5-*acetate*,

$$CH_2\!<\!\begin{matrix}CMe\!=\!=\!CH\\CHMe\text{-}CH_2\end{matrix}\!>\!C(OH)\cdot CH_2\cdot CO_2R,$$

b. p. 110°/2·5 mm. or 123°/4·5 mm. (decomp.), $D_4^{16\cdot8}$ 1·0126, $n_\alpha^{17\cdot6}$ 1·46857, $n_D^{17\cdot6}$ 1·47133, $n_\gamma^{17\cdot6}$ 1·48411 (whence $\Sigma_\alpha = +0\cdot27$, $\Sigma_D + 0\cdot20$, and $\Sigma_\gamma - \Sigma_\alpha = 7\%$), is a colourless, viscid oil, which when heated with dehydrating agents furnishes *ethyl* 1 : 3-*dimethyl*-Δ^3-cyclo*hexenylidene*-5-*acetate*, $CH_2\!<\!\begin{matrix}CMe\!=\!=\!CH\\CHMe\text{-}CH_2\end{matrix}\!>\!C\!:\!CH\cdot CO_2Et$, b. p. 111—113°/5·5 mm. or 145—147°/15 mm., D_4^{20} 0·971—0·979, n_α^{20} 1·510—1·513, n_D^{20} 1·516—1·519, $\Sigma_\alpha + 1\cdot79$ to 2·15, $\Sigma_D + 1\cdot87$ to 2·25, and $\Sigma_\gamma - \Sigma_\alpha$ 116 to 123%, which is identical with the substance wrongly assumed by Wallach and Bötticher to be ethyl $\Delta^{1:5}$-dihydro-3 : 5-xylyl-1-acetate, $CH_2\!<\!\begin{matrix}CMe\!=\!CH\\CHMe\text{-}CH\end{matrix}\!>\!C\cdot CH_2\cdot CO_2Et$ (Abstr., 1902, i, 798). On hydrolysis with sodium ethoxide, it yields the free acid,

m. p. 153—154°, and this when heated in closed tubes furnishes the corresponding hydrocarbon, 1 : 3-dimethyl-5-methylene-Δ^3-*cyclo*hexene (this vol., i, 826, and Wallach and Böttcher, *loc. cit.*). The acid is reduced with sodium amalgam in presence of carbon dioxide to 1 : 3-*dimethyl*-Δ^4-cyclo*hexene*-5-*acetic acid*, b. p. 154—155°/16·5 mm., $D_4^{20\cdot1}$ 0·9947, n_α 1·47428, n_D 1·47731, n_γ 1·49068 (whence $\Sigma_\alpha + 0\cdot33$, $\Sigma_D + 0\cdot27$, and $\Sigma_\gamma - \Sigma_\alpha = 8\%$), a colourless oil, which is oxidised by permanganate to an *acid*, $C_9H_{15}O_3$, and on treatment with bromine followed by sodium hydroxide solution yields *s*-xylylacetic acid.

Ethyl 1 : 3-dimethyl-Δ^3-*cyclo*hexenylidene-5-acetate when treated with magnesium methyl iodide yields 1 : 3-*dimethyl*-Δ^3-cyclo*hexene*-5 *trimethylcarbinol*, $CH_2<\begin{matrix}CMe=\!=CH\\CHMe\text{-}CH_2\end{matrix}>C{:}CH\cdot CMe_2\cdot OH$, b. p. 125—126°/18 mm., D_4^{20} 0·922—0·934, n_α^{20} 1·503—1·506, n_D^{20}, 1·508—1·510 (whence $\Sigma_\alpha = +0\cdot95$ to $+1\cdot23$, $\Sigma_D = +1\cdot00$ to 1·28, and $\Sigma_\gamma - \Sigma_\alpha = 48\%$), which, since it decomposes on heating, could not with certainty be prepared free from the *hydrocarbon*,

$$CH_2<\begin{matrix}CMe=\!=CH\\CHMe\text{-}CH_2\end{matrix}>C{:}CH\cdot CMe{:}CH_2,$$

resulting from this decomposition. This hydrocarbon has b. p. 103—106°/17 mm., D_4^{20} 0·862—0·867, n_α^{20} 1·495—1·518, n_D^{20} 1·503—1·533, Σ_α +0·72 to 1·86, Σ_D +0·75 to 2·02, and $\Sigma_\gamma - \Sigma_\alpha$ +25 to 93%. T. A. H.

Bismuth Benzoates. Godfrin (*J. Pharm. Chim.*, 1910, [vii], 2, 385—396. Compare Rebière, Abstr., 1896, ii, 396).—Bismuth benzoate and a series of basic bismuth benzoates are described, full details of their method of preparation being given.

Bismuth benzoate, $Bi(OBz)_3$, prepared by double decomposition between bismuth nitrate and sodium benzoate, both salts being dissolved in a mixture of water and glycerol, and a solution of benzoic acid in water being used for washing and re-crystallising the salt, forms bulky, brilliant, colourless, orthorhombic prisms, is stable up to 140°, and is decomposed by water, alcohol, or ether, forming basic salts. Treated in the cold with twenty times its weight of alcohol it furnishes a salt, $Bi_4O_3(OBz)_6$. This is a dead white powder, seen under the microscope to consist of minute, colourless, cubic crystals. It decomposes at about 160°. When treated with twenty times its weight of cold ether or a like quantity of alcohol at 95°, the neutral salt yields a new basic *salt*, $Bi_2O_3(BiO\cdot OBz)_{12}$, a white, partly crystalline powder. All the foregoing when treated with alcohol at 95° furnish the *salt*, $Bi_2O_3(BiO\cdot OBz)_6$, which consists of colourless, microscopic, monoclinic prisms. *Bismuthyl benzoate*, BiO·OBz, crystallises in minute, monoclinic prisms. It is stable in air up to 140°, but when treated with alcohol at 95° it decomposes, like the other salts described, furnishing the salt $Bi_2O_3(BiO,OBz)_6$. T. A. H.

Alkylation of Aromatic Amino-acids. IV. Nitroamino- and Iodoamino-acids. Henry L. Wheeler and Carl O. Johns (*Amer. Chem. J.*, 1910, 44, 5, 441—452. Compare this vol. i, 381, 666).—The investigation of the behaviour of aromatic amino-acids on

ethylation is continued by a study of further acids. 4-Nitro-2-aminobenzoic acid gives a mixture of 40% of the primary amino-ester and 40% of the *N*-alkyl acid. 2-Nitro-4-aminobenzoic acid gives only the ester (43·4%). Both 4-iodo-*o*-aminobenzoic acid and 5-iodo-*o*-aminobenzoic acid give only *N*-alkyl acids (71—76%). 4 : 5-Di-iodo-*o*-aminobenzoic acid alkylates with difficulty, and gives only the ester (28%).

These results show that the tendency of amino-acids to react in an abnormal manner and give esters is not dependent on stereochemical interference.

An improved method for the preparation of 4-nitro-2-aminobenzoic acid is given; the ethyl ester melts at 100°.

4-*Iodo*-2-*nitrobenzoic acid* forms prisms, m. p. 192°. 4-*Iodo*-2-*aminobenzoic acid* crystallises in flat prisms, decomposing at 208°; 4-*iodo*-2-*ethylaminobenzoic acid* forms clusters of plates, m. p. 188°. 4-*Iodo*-2-*methylaminobenzoic acid* crystallises in needles, m. p. 197°.

4 : 5-*Di-iodo*-2-*aminobenzoic acid* begins to give off iodine at 200°; its *ethyl* ester forms slender needles, m. p. 137°. N. C.

Complete Methylation of Some Amino-acids. R. Engeland (*Ber.*, 1910, **43**, 2662—2664. Compare Abstr., 1909, i, 856).—When a mixture of phenylalanine (α-amino-β-phenylpropionic acid), methyl-alcoholic potassium hydroxide, and methyl iodide is boiled gently for several hours, the chief product is *phenyl*-N-*trimethylalanine methyl* ester, the *platinichloride* of which, $2C_{13}H_{20}O_2NPtCl_6$, has m. p. 177—178°. The *aurichloride* of *phenyltrimethylalanine*,

$$C_{12}H_{18}O_2N,HAuCl_4,$$

forms golden-yellow needles, m. p. 94—95°.

When α-aminoglutaric acid is treated in a similar manner two products are obtained, the one forms a sparingly soluble *aurichloride*, $C_9H_{17}O_4N,HAuCl_4$, probably derived from the dimethyl ester of dimethylglutamic acid, and the other an *aurichloride*,

$$C_7H_{13}O_4N,HAuCl_4,$$

in the form of readily soluble, hygroscopic crystals, probably derived from dimethylglutamic acid. J. J. S.

Synthesis of Compounds of the Normal Phenylpropane, Phenylbutane, and Phenylpentane Series. Julius von Braun (*Ber.*, 1910, **43**, 2837—2852).—The synthesis of compounds containing the group $C_6H_5\cdot[CH_2]_x\cdot$ is important, since it is very probable that many resins contain such fatty-aromatic chains. Methods based on the interaction of sodium and aryl halides, or of aluminium chloride and aromatic hydrocarbons, on substances of the type

$$Cl\cdot[CH_2]_x\cdot Cl$$

or $Cl\cdot[CH_2]_x\cdot OPh$ have proved unsatisfactory. γ-Bromopropylphthalimide and ε-chloroamylphthalimide are very resistent to the attack of sodium, but, contrary to expectation, react with aluminium chloride. The former yields only an additive compound, which is easily decomposed into its generators, but its formation suggests that the usual Friedel-Crafts' reaction might take place with a substance in which the acylated amino-group is removed further from the

halogen atom. This expectation is fulfilled, benzoyl-ε-chloroamylamine and benzoyl-ζ-chlorohexylamine reacting with aluminium chloride and benzene in the usual way. The product of the first reaction is *benzoyl-ε-phenylamylamine*, $C_6H_5\cdot[CH_2]_5\cdot NHBz$, b. p. 273—275°/15 mm., in 90% yield, which is hydrolysed by hydrochloric acid under pressure to *ε-phenylamylamine*, b. p. 131°/15 mm., a colourless liquid which has a faint basic odour, only slowly absorbs water and carbon dioxide from the air, and forms a *platinichloride*,

$$2C_{11}H_{17}N,H_2PtCl_6,$$

decomp. 220°, *picrate*, m. p. 152—153°, *benzoyl* derivative, m. p. 60° (the benzoyl derivative, as obtained in the preparation above, has not been made to crystallise), and a *methiodide*,

$$C_6H_5\cdot[CH_2]_5\cdot NMe_2,MeI,$$

m. p. 181°, the *platinichloride* of which has m. p. 219°. The normal constitution of the ε-phenylamylamine, prepared from benzoyl-ε-chloroamylamine by the Friedel-Crafts' method, is proved by the synthesis of the base by the following series of reactions, which represent the fulfilment of the object of the author's work. *γ-Iodopropylbenzene*, $C_6H_5\cdot[CH_2]_3I$, b. p. 137—140°/20 mm., obtained by the prolonged boiling of γ-chloropropylbenzene and sodium iodide in alcohol, is warmed with an aqueous alcoholic solution of potassium cyanide (2 mols.), whereby *γ-phenylbutyronitrile*, b. p. 142—145°/16 mm., is obtained; the nitrile, by reduction with sodium and alcohol (distilled over sodium and kept for many days, or, better, weeks over calcium), yields *δ-phenylbutylamine*, $C_6H_5\cdot[CH_2]_4\cdot NH_2$, b. p. 123—124°/17 mm. (*platinichloride*, decomp. 205°; *picrate*, m. p. 125°; the *N-dimethyl methiodide*, $C_6H_5\cdot[CH_2]_4\cdot NMe_2,MeI$, m. p. 191—192°), the *benzoyl* derivative of which, m. p. 83·5°, is converted by distillation with phosphorus pentachloride into *δ-chlorobutylbenzene*,

$$C_6H_5\cdot[CH_2]_4\cdot Cl,$$

b. p. 122—123°/17 mm., in 75% yield. This substance, by reactions similar to the preceding, is converted successively into *δ-iodobutylbenzene*, b. p. 148—151°/15 mm., *δ-phenylvaleronitrile*, b. p. 157—161°/17 mm., and ε-phenylamylamine, which is identical with the base prepared above.

By distillation with phosphorus pentachloride, benzoyl-ε-phenylamylamine yields *ε-chloroamylbenzene*, $C_6H_5\cdot[CH_2]_5Cl$, b. p. 134°/18 mm., which has a very pleasant odour, reacts with alcoholic sodium phenoxide to form *phenyl ε-phenylamyl ether*, b. p. 198°/14 mm., and with alcoholic sodium iodide to form *ε-iodoamylbenzene*, b. p. 158—165°/20 mm., in which the presence of the normal amyl chain is proved by the reaction of the iodide with alcoholic trimethylamine, whereby ε-phenylamyltrimethylammonium iodide, m. p. 181°, is obtained, identical with the salt produced by the exhaustive methylation of ε-phenylamylamine.

γ-Chloropropylbenzene is obtained readily from tetrahydroquinoline. The benzoylated base is ruptured by phosphorus pentachloride, and the resulting *o*-γ-chloropropylbenzanilide is hydrolysed to γ-chloropropylaniline, from which the amino-group is eliminated by diazotisation and subsequent treatment with alkaline stannous chloride. γ-Bromopropylbenzene, which is obtained quantitatively from dihydro-

cinnamyl alcohol and fuming hydrobromic acid at 105°, can only be prepared indirectly from γ-chloropropylbenzene; the latter is boiled for many hours with a large excess of alcoholic sodium phenoxide, and the resulting *phenyl γ-phenylpropyl ether*, $CH_2Ph\cdot[CH_2]_2\cdot OPh$, b. p. 182—183°/17 mm., is heated with fuming hydrobromic acid.

C. S.

The Liberation of Carbon Monoxide from the Tertiary Acids Arising from the Condensation of Phenylpyruvic Acid with Aromatic Hydrocarbons. Augustin Bistrzycki and Louis Mauron (*Ber.*, 1910, **43**, 2883—2889. Compare Abstr., 1907, i, 1039; Bistrzycki and von Weber, this vol., i, 742).—The investigation of the liberation of carbon monoxide from tertiary acids on treatment with concentrated sulphuric acid has now been extended to some benzyldiarylacetic acids, which have now been prepared from phenylpyruvic acid and aromatic hydrocarbons, using cooled, concentrated sulphuric acid as the condensing agent, in the manner previously described (Bistrzycki and Reintke, Abstr., 1905, i, 285). The acids of this type evolve only two-thirds to three-quarters of the theoretical amount of carbon monoxide, the incompleteness of the reaction being due probably to partial sulphonation. The products obtained are completely soluble in water. Triarylethylenes, analogous to the diarylethylenes of Bistrzycki and Reintke (*loc. cit.*), were not obtained. None of the acids loses carbon dioxide on heating.

β-Phenyl-αα-di-p-*tolylpropionic acid*, $CH_2Ph\cdot C(C_6H_4Me)_2\cdot CO_2H$, from toluene and phenylpyruvic acid, crystallises in colourless, lustrous needles or prisms, m. p. 176°. That the phenylpyruvic acid has not reacted in the desmotropic form (compare Ruhemann and Stapleton, Trans., 1900, **77**, 241) follows from the fact that the analogous anisole derivative yields di-*p*-anisyl ketone on oxidation (Lamoni, *Diss.* Freiburg, Switzerland, 1910, 33). The *silver* salt, $C_{23}H_{21}O_2Ag$, was obtained as a white precipitate. The *methyl* ester, $C_{24}H_{24}O_2$, forms hexagonal prisms, m. p. 117°.

α-Phenyl-ββ-di-p-*ethylphenylpropionic acid*,

$$CH_2Ph\cdot C(C_6H_4Et)_2\cdot CO_2H$$

(from ethylbenzene), crystallises in rosettes of stout needles or in flat prisms, m. p. 183—184°. The *ethyl* ester, $C_{27}H_{30}O_2$, forms microscopic prisms, m. p. 61°.

α-Phenyl-ββ-di-o-xylylpropionic acid, $CH_2Ph\cdot C(C_6H_3Me_2)\cdot CO_2H$ (from *o*-xylene), crystallises in four-sided prisms or in needles, m. p. 160°. The *methyl* ester, $C_{26}H_{28}O_2$, forms microscopic prisms, m. p. 96—97°.

Phenylpyruvic acid does not react with *m*-xylene under the conditions stated, or with mesitylene and naphthalene. Only in one instance was it possible to obtain with benzene an acid of the m. p. of the expected *αββ*-triphenylpropionic acid, whilst the products from cumene and cymene were difficult to purify. R. V. S.

Comparison of Certain Acids Containing a Conjugated System of Double Linkings. Annie Louise Macleod (*Amer. Chem. J.*, 1910, **44**, 331—352).—Reimer (Abstr., 1907, i, 852) has

shown that when methyl cinnamylidenemalonate is treated with a Grignard reagent, $\alpha\delta$-addition takes place, but on decomposing the product rearrangement occurs, and the hydrogen atom by which the magnesium has been replaced is found to occupy the α-position to the carboxyl group. Reimer and Reynolds (Abstr., 1908, i, 988) have shown that methyl α-phenylcinnamylideneacetate reacts less readily with organic magnesium compounds, and that the resulting products consist chiefly of ketones formed by the replacement of the methoxy-group and subsequent addition of a second molecule of the reagent in the $\alpha\delta$-position. A study has now been made of α-methylcinnamylidenacetic and α-cyanocinnamylideneacetic acids.

α-Methylcinnamylidenacetic acid is pale yellow when first obtained, but becomes white on exposure to light. It has been found that when the yellow form is treated with a very small quantity of sodium amalgam, the yellow colour disappears, and the colourless acid remains. The substance to which the yellow colour is due is therefore present in only small amount, and may possibly be an isomeric form of the acid. When the acid is exposed to direct sunlight for about four days, it is converted into 2 : 4-*diphenyl*cyclo*butane*-1 : 3-*di-α-methyl-acrylic acid*, $CO_2H\cdot CMe{:}CH\cdot CH<^{CHPh}_{CHPh}>CH\cdot CH{:}CMe\cdot CO_2H$, m. p. 253—254°, which forms small, transparent prisms, and, on oxidation with potassium permanganate, yields α-truxillic, benzoic, and oxalic acids; its *methyl* ester, m. p. 126·5—127°, crystallises in slender needles. The acid unites with bromine with formation of a product which appears to be a mixture of a di- and a tetra-bromide; the methyl ester gives a *tetrabromide*, m. p. 200—201°.

When methyl α-methylcinnamylideneacetate is treated with bromine in presence of a little iodine, a *tetrabromide*, m. p. 128°, is produced, whilst, in the absence of iodine, a *dibromide*, m. p. 81°, is obtained, which liberates iodine from alcoholic potassium iodide, thus showing that the bromine atoms are attached to adjacent carbon atoms. When a solution of this dibromide in acetone is oxidised with potassium permanganate in presence of acetic acid, small quantities of a *substance*, m. p. 131°, are produced, which contains halogen, but does not liberate iodine from alcoholic potassium iodide.

Ethyl α-cyanocinnamylideneacetate reacts readily with organic magnesium compounds with production of quantitative yields of $\alpha\delta$-additive compounds. When this ester (1 mol.) is treated with magnesium ethyl bromide ($2\frac{1}{2}$ mols.) and the product is decomposed with hydrochloric acid, *ethyl α-cyano-δ-phenyl-β-ethyl-Δγ-pentenoate*, $CHPh{:}CH\cdot CHEt\cdot CH(CN)\cdot CO_2Et$, b. p. 220°/20 mm., is obtained as a yellow oil; on hydrolysis with potassium hydroxide, the *potassium* salt is obtained, from which the *acid* separates on the addition of hydrochloric acid as an uncrystallisable oil. On heating this acid with alcoholic potassium hydroxide for two days, it is converted into *δ-phenyl-β-ethylallylmalonamic acid*,

$$CHPh{:}CH\cdot CHEt\cdot CH(CO\cdot NH_2)\cdot CO_2Et,$$

m. p. 165°, which, when heated above its m. p., yields *δ-phenyl-β-ethyl-Δγ-pentenoamide*, $CHPh{:}CH\cdot CHEt\cdot CH_2\cdot CO\cdot NH_2$, m. p. 101°, which forms slender needles.

Ethyl α-cyanocinnamylideneacetate reacts with magnesium phenyl bromide to form *ethyl α-cyano βδ-diphenyl-Δγ-pentenoate*,

$$CHPh{:}CH{\cdot}CHPh{\cdot}CH(CN){\cdot}CO_2Et,$$

b. p. 263°/18 mm.

Both α-cyano- and α-methyl-cinnamylideneacetic acids react readily with potassium hydrogen sulphite, yielding colourless, additive compounds which could not be isolated. E. G.

Unsaturated Compounds. VIII. Addition of Hydroxylamine to Unsaturated Acids containing Conjugate Double Linkings. Theodor Posner and Karl Rohde (*Ber.*, 1910, 43, 2665—2676. Compare Abstr., 1909, i, 583, 649; Riedel and Schulz, *ibid.*, i, 581).—In further proof of the constitution of β-benzoylamino-β-styrylpropionic [β-benzoylamino-δ-phenyl-Δγ-pentenoic] acid is adduced the fact that on oxidation benzoylaspartic acid is formed. Although β-benzoylamino-δ-phenyl-Δγ-pentenoic acid and its ester contain olefinic linkings, it has not been found possible to form additive compounds with hydroxylamine or bromine. The addition of hydroxylamine to styrylacrylic acid proceeds slowly, for example, 240 hours' boiling of the solution is required, whereas with cinnamic acid five hours is sufficient.

The addition of hydroxylamine to sorbic, piperic, and α-phenylstyrylacrylic acids and their esters has been studied. The compounds combine with hydroxylamine (compare Riedel and Schulz, *loc. cit.*): sorbic acid at much the same rate as styrylacrylic acid, piperic acid much less readily, as also α-phenylstyrylacrylic acid and all α-alkylated unsaturated acids.

β-Amino-δ-phenyl-Δγ-pentenoic acid can be obtained by prolonged boiling of β-hydroxylamino-δ-phenyl-Δγ-pentenohydroxamoxime hydrate (Abstr., 1909, i, 649) with methyl alcohol. It has not been found possible to prepare Riedel and Schulz's β-hydroxylamino-δ-phenyl-Δγ-pentenohydroxamic acid by the method they give; the product formed under these conditions is *styrylacrylhydroxamic acid*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}C(OH){:}N{\cdot}OH,$$

m. p. 146°.

Methyl sorbate, $CHMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me$, is a colourless liquid with a pleasant odour, and has b. p. 180°/759 mm. The ester reacts with a cold solution of hydroxylamine in methyl alcohol during the course of a week, yielding an oil which is probably *β-hydroxylaminohydrosorbhydroxamoxine hydroxide*. *Aminohydrosorbic acid* (*β-amino-Δγ-hexenoic acid*) is formed when the above hydroxide is boiled with methyl alcohol, or when a mixture of the methyl ester and hydroxylamine is boiled for ten hours with methyl alcohol. The same product is also formed when free sorbic acid is used, but the boiling must then be continued for 240 hours; it is an oil, and yields a *benzoyl* derivative, $CHMe{:}CH{\cdot}CH(NH{\cdot}COPh){\cdot}CH_2{\cdot}CO_2H$, which crystallises from alcohol, and has m. p. 152°.

Methyl piperate, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me$, is deposited from methyl alcohol in glistening crystals, m. p. 146°, and reacts with a hot methyl-alcoholic solution of hydroxylamine, yielding *β-amino-α-hydropiperic acid* (*β-amino-δ-3 : 4-methylenedioxyphenyl-Δγ-pentenoic*

acid), $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2H$, which crystallises from water in colourless needles, m. p. 231° (decomp.). A small amount of the same product is also formed when sorbic acid itself is used; it yields a *benzoyl* derivative, $C_{19}H_{17}O_5N$, m. p. 188°, and reacts with potassium cyanate, forming *β-carbamido-α-hydropiperic acid*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH(NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}CO_2H$, as glistening crystals, m. p. 211°. The carbamido-acid, when heated at 215°, yields 3 : 4-*methylenedioxystyryldihydrouracil*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{<}\begin{matrix}CH_2{\cdot}CO\\NH{-}CO\end{matrix}{>}NH,$$

as a yellow, crystalline powder, m. p. 224°.

Methyl α-phenylstyrylacrylate, $CHPh{:}CH{\cdot}CH{:}CPh{\cdot}CO_2Me$, forms yellow crystals, m. p. 79—80°, and when boiled for several days with hydroxylamine and methyl alcohol yields *β-amino-αδ-diphenyl-Δγ-pentenoic acid*, $CHPh{:}CH{\cdot}CH(NH_2){\cdot}CHPh{\cdot}CO_2H$, which crystallises from water in colourless needles, m. p. 200° (decomp.). The *benzoyl* derivative, $C_{24}H_{21}O_3N$, forms colourless, glistening crystals, m. p. 222·5°, and *β-carbamido-αδ-diphenyl-Δγ-pentenoic acid*,

$$CHPh{:}CH{\cdot}CH(NH{\cdot}CO{\cdot}NH_2){\cdot}CHPh{\cdot}CO_2H,$$

colourless, glistening needles, m. p. 197°; the corresponding 5-*phenyl*-4-*styryldihydrouracil*, $CHPh{:}CH{\cdot}CH{<}\begin{matrix}CHPh{\cdot}CO\\NH{-}{-}CO\end{matrix}{>}NH$, forms a pale yellow powder, m. p. 212·5°, after softening at 192°.

When cinnamylidenemalonic acid is heated with methyl alcohol and hydroxylamine, carbon dioxide is evolved, and β-amino-δ-phenyl-Δγ-pentenoic acid is formed, whereas the corresponding methyl ester reacts with a methyl-alcoholic solution of hydroxylamine at 0°, yielding a crystalline product, m. p. 72°, which is probably a hydroxylamino-hydroxamoxime hydroxide. J. J. S.

A New Step in the Reduction of the Nitro-group. III. Gustav Heller and Friedrich Frantz (*Ber.*, 1910, **43**, 2892—2899. Compare Abstr., 1906, i, 585; 1908, i, 208).—Since in the numerous cases examined it has not been possible to obtain the compound containing a dihydroxylamine group, which is the first product of the reduction of *o*-nitromandelonitrile, substituted mandelonitriles have now been investigated. Of these, 5-chloro-2-nitromandelonitrile does not yield the characteristic molecular compound in solid form, although its presence in the liquid can be shown by the production of 5-chloroisatin on acetylation. In the case of 5-bromo-2-nitromandelonitrile, the desired substance is obtainable in the form of its hydrochloride, although with a poor yield, and its reactions correspond in all respects with the observations previously recorded. A further proof of the existence of the combination of di- and mono-hydroxylamine compounds follows from the fact that solutions of the above hydrochloride when kept deposit 5-bromo-2-nitrosomandelonitrile, so that evidently no tendency to the formation of an azoxy-compound exists.

5-Chloro-2-nitromandelonitrile, $C_8H_5O_3N_2Cl$, is prepared by adding a concentrated, aqueous solution of potassium cyanide to a solution of 5-chloro-2-nitrobenzaldehyde (Einhorn and Eichengrün, Abstr., 1891, 1098) in glacial acetic acid, or by adding the aldehyde to twice its weight of anhydrous hydrocyanic acid. It forms rosettes

of needles, m. p. 85°, and also large prisms containing chloroform of crystallisation, m. p. 64—66°.

5-Chloro-2-nitromandelic acid, $C_8H_6O_5NCl$, m. p. 134°, is obtained by evaporating the nitrile with twenty times its weight of hydrochloric acid almost to dryness. The *methyl* ester, $C_9H_8O_5NCl$, has m. p. 87—88°. With alcoholic ammonia, 5-chloro-2-nitromandelonitrile yields the *ammonium* salt of *5-chloro-2-nitrosobenzoic acid*, which may be obtained from it by the action of dilute hydrochloric acid. The free acid crystallises in colourless needles, which become coloured towards 170° and melt at 179°. After reduction with zinc and acetic acid no precipitate was observed, but on addition of hydrochloric acid and acetic anhydride a dark-coloured oil separated, and the solution when kept yielded 5-chloroisatin. The oil was insoluble in cold sodium hydroxide, and therefore was not 5-chloro-*N*-acetoxyisatin.

5-Bromo-2-nitromandelonitrile, prepared from 5-bromo-2-nitrobenzaldehyde, has m. p. 81°. When it is reduced with zinc and acetic acid in an atmosphere of hydrogen, the liquid being cooled with water and well stirred, the molecular compound of *5-bromo-2-mono-* and *5-bromo-2-di-hydroxylaminomandelonitrile hydrochloride*, $C_{16}H_{16}O_5N_4Cl_2Br_2$, separates. After purification by precipitation with concentrated hydrochloric acid from solution in weaker acid, it crystallises in a mass of colourless, crooked needles, which become coloured at 130° and decompose towards 145°. The free compound can also be isolated. On keeping, an aqueous solution of the hydrochloride deposits a brown precipitate, which, when saponified with dilute sodium hydroxide, yields bromoanthroxanic acid and bromoisatin. These substances are obtained directly by heating the salt with concentrated hydrochloric acid. *5-Bromoisatin*, $C_8H_4O_2NBr$, forms yellow needles, m. p. 255°. *5-Bromoanthroxanic acid*, $C_8H_4O_3NBr$, crystallises in colourless needles. It melts at 202—203°, with evolution of gas and partial sublimation; the yellow residue darkens on further heating, and melts towards 253° with evolution of gas. Bromoanthroxanic acid is reduced by ammoniacal ferrous sulphate, and on acidification 5-bromoisatin is precipitated. The hydrochloride of the molecular compound yields on treatment with dilute sodium hydroxide a colourless *compound*, m. p. 186—187°, and an aminocarboxylic acid, probably *5-bromo-2-aminomandelic acid*, crystallising in colourless needles, which become coloured towards 230°. Acetylation of the molecular compound in presence of an excess of hydrochloric acid gives rise to 5-bromo-1-acetoxyisatin. Phenylhydrazine reacts with the hydrochloride, yielding 5-bromo-1-hydroxyisatinphenylhydrazone and *5-bromoisatin-2-phenylhydrazone*, $C_{14}H_{10}ON_3Br$, which forms dark red crystals, m. p. 242—243°.

5-Bromo-2-nitrosomandelonitrile, $C_8H_5O_2N_2Br$, which can be obtained (in addition to 5-bromoisatin) from the filtrate from the molecular compound in the preparation of the latter, crystallises in compact, colourless prisms, m. p. 225—226°. On hydrolysis it yields 5-bromoanthroxanic acid. R. V. S.

Action of Amines on Phthalic Acid. VII. J. Bishop Tingle and S. J. Bates (*J. Amer. Chem. Soc.*, 1910, **32**, 1319—1330).—In continuation of the work on the interaction of amines with phthalic

acid and its derivatives (Abstr., 1907, i, 692, 1044; 1909, i, 28, 798, 909; this vol., i, 263), a study has been made of phthalamic acids containing one or more chlorine atoms or nitro-groups in the benzene nucleus.

Di-m-*toluidine* and *di*-p-*chloroaniline* 3 : 6-*dichlorophthalates*, m. p. 176° and 215° respectively, form pale yellow crystals. An improved method is described for the preparation of 3 : 6-dichlorophthalanilic acid and its anil. The anil has m. p. 201°, and not 191° as stated by Graebe (Abstr., 1900, i, 547). The acid is not affected by solutions of amines in benzene, but is readily converted into the anil by the action of 50% alcohol. This dehydrating action of alcohol has been discussed by Tingle and Rolker (Abstr., 1909, i, 29).

Tetrachlorophthal-o-*toluidic acid*, $C_6H_4Me\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p. 218—220°, obtained by the action of *o*-toluidine on tetrachlorophthalic acid or anhydride, forms white, lustrous crystals.

Tetrachlorophthalanilic acid, $NHPh\cdot CO\cdot C_6Cl_4\cdot CO_2H$, m. p. 266°, obtained by boiling tetrachlorophthalanil (Graebe and Buenzod, Abstr., 1899, i, 763) with solution of potassium hydroxide or by the action of aniline on tetrachlorophthalic anhydride, forms white crystals; its *sodium* and *potassium* salts are colloidal, and yield soapy solutions. *Tetrachlorophthalo-β-naphthylamic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot C_6Cl_4\cdot CO_2H$, m. p. 287°, forms white crystals, and yields colloidal *sodium* and *potassium* salts. When the acid is heated for ten minutes at 260—270°, it is converted into the *β-naphthylimide*, $C_6Cl_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_{10}H_7$, m. p. 287°, which is a white, crystalline substance.

When 3-nitrophthalanilic acid, $NHPh\cdot CO\cdot C_6H_3(NO_2)\cdot CO_2H$, is heated at 100° with 50% alcohol, it is slowly transformed into a 3-*nitrophthalodianilide*, m. p. 233—234°, which appears to be isomeric with that obtained by Chambers (Abstr., 1903, i, 699) of m. p. 211—212°. 3-*Nitrophthalo-β-naphthylamic acid*,

$$C_{10}H_7\cdot NH\cdot CO\cdot C_6H_3(NO_2)\cdot CO_2H,$$

m. p. 201—202°, obtained by the action of *β*-naphthylamine on 3-nitrophthalic anhydride, forms light yellow crystals.

4-Nitrophthalanilic acid, obtained by heating the anil (Graebe and Buenzod, *loc. cit.*) with solution of potassium hydroxide or by treating aniline with 4-nitrophthalic anhydride, has m. p. 192°, and not 181° as stated by Bogert (Abstr., 1902, i, 98). The anil has m. p. 200—201° (Bogert gives 194°). When 4-nitrophthalanilic acid is heated at 100° with 50% alcohol, it is partly transformed into the anil; in presence of aniline the same product is obtained, together with a small quantity of a *compound*, m. p. 199—200°, which is probably 4-nitrophthalodianilide, $NO_2\cdot C_6H_3(CO\cdot NHPh)_2$.

On comparing the results of the transformation experiments with 3- and 4-nitrophthalanilic acids, it is evident that the approximation of negative groups ($CO_2H:CO_2H:NO_2 = 1:2:3$) inhibits the formation of the anil and greatly favours that of the dianilide, whereas the reverse is the case when the nitro-group is in the 4-position. 4-*Nitrophthalo-β-naphthylamic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot C_6H_3(NO_2)\cdot CO_2H$, m. p. 202—204°, prepared by the action of *β*-naphthylamine on 4-nitrophthalic anhydride, forms pale yellow crystals.

Camphoro-β-naphthylamic acid, $C_{10}H_7\cdot NH\cdot CO\cdot C_8H_{14}\cdot CO_2H$, m. p. 220—221°, obtained by the action of β-naphthylamine on camphoric anhydride, and camphoranilic acid (Auwers, Abstr., 1900, i, 85) are not affected by prolonged heating with amines or with 50% alcohol.

E. G.

Synthesis of Ethyl *cyclo*Butanehexacarboxylate. Yugi Shibata (*Ber.*, 1910, 43, 2619—2622).—*Ethyl* cyclo*butanehexacarboxylate*, $(CO_2Et)_2C<\begin{matrix}C(CO_2Et)_2\\CH(CO_2Et)\end{matrix}>CH\cdot CO_2Et$, can be synthesised by the action of the disodium derivative of ethyl ethanetetracarboxylate (Bischoff and Rach, Abstr., 1885, 244) on ethyl dibromosuccinate (Gorodetzky, Abstr., 1888, 820) in the presence of dry ether at 0° and with vigorous automatic stirring. It crystallises from alcohol in large, monoclinic plates [$a:b:c=1\cdot565:1:1\cdot542$; $\beta=131°32'$], m. p. 80°. Unaltered ethyl ethanetetracarboxylate is deposited with the *cyclo*butane derivative, but can be removed mechanically, as it forms large, needle-shaped crystals.

An oily by-product formed during the condensation is Bischoff's ethyl ethylenetetracarboxylate, $C(CO_2Et)_2{:}C(CO_2Et)_2$. The condensation does not take place when the reagents are heated in sealed tubes at 120—130°, and the same products are formed when ethyl *iso*dibromosuccinate is used.

J. J. S.

Rotatory Power of Usnic Acid and other Lichen Derivatives. III. Heinrich Salkowski (*Annalen*, 1910, 377, 123—126. Compare Abstr., 1901, i, 152; 1902, i, 228).—The values for $[\alpha]_D^t$ for the following substances are given: *d*-Usnic acid (from nineteen species of lichens), +461·9° to +521·9°; *l*-usnic acid (from thirteen species), −455·9° to −496·8°; kamschadalic acid, +26·42°; lepranthin, +70·5°; pleopsidic acid, −66·15°; protolichenosteric acid, +12·1°.

Barbatic acid, lecanarolic acid, and salazinic acid appear to be inactive.

In most cases chloroform solutions were used.

Gymnogrammen from *Gymnogramme chrysophylla* has an orange colour, m. p. 159°, and $[\alpha]_D^{18}$ +12°.

J. J. S.

Ethyl Tannate. Rodger J. Manning (*J. Amer. Chem. Soc.*, 1910, 32, 1312—1319).—The composition of gallotannic acid has hitherto been uncertain, owing to the fact that crystalline derivatives were not known, and the substance was therefore difficult to purify. The ethyl ester has now been prepared in two crystalline forms with different amounts of water of crystallisation.

On treating an alcoholic solution of gallotannic acid with dry hydrogen chloride, *ethyl gallotannate*, $C_{51}H_{52}O_{26},5H_2O$, m. p. 157°, is obtained in the form of nodules of pale yellow, lustrous crystals. When hydrolysed with dilute hydrochloric acid or dilute potassium hydroxide, it yields ethyl alcohol, dextrose, and gallic acid. Estimations of the gallic acid and dextrose, and determinations of the molecular

weight by the ebullioscopic method have shown that ethyl gallotannate has the composition $C_{41}H_{27}O_{21}(OEt)_5,5H_2O$, and that it is a glucoside in which one formula weight of dextrose and five formula weights of gallic acid are represented in one molecule of the ester. Gallotannic acid is therefore represented by the formula $C_{41}H_{27}O_{21}(OH)_5$.

The ester was synthesised by treating a mixture of ethyl gallate and dextrose with phosphoryl chloride.

If a saturated solution of the ester is allowed to evaporate at the ordinary temperature, large, pale brown crystals are obtained of the composition $C_{51}H_{52}O_{26},15H_2O$, m. p. 132°. E. G.

Theory of the Phenomena of Halochromy. I. Additive Compounds of Tin Halogenides and Carbonyl Compounds. Paul Pfeiffer [with O. Halperin, E. Pros, and V. Schwarzkopf] (*Annalen*, 1910, **376**, 285—310).—The first step in the elucidation of the constitution of the coloured additive compounds of organic substances and metallic salts and acids, and therewith the nature of the phenomenon of halochromy, must be a systematic examination of the additive capacity of simply constituted substances. Since halochromy is most frequently observed in connexion with carbonyl compounds, these have been selected as the organic components; the inorganic are tin tetrachloride and tetrabromide, which have the property of forming well-characterised molecular compounds of simple composition.

The additive compound is obtained by bringing the tin halogenide and the carbonyl compound (aldehyde, ketone, acid, ester, or amide, containing generally the benzoyl or cinnamoyl group; acid chlorides do not form additive compounds) together in anhydrous ether, benzene, or chloroform; in the case of liquid esters, a solvent is dispensed with. In this way have been prepared the following colourless compounds: $SnCl_4,2PhCHO$, m. p. 187—189°; $SnBr_4,2PhCHO$, m. p. 127—128°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CHO$, m. p. 225—230°; $SnBr_4,2CHPh{\cdot}CH{:}CH{\cdot}CHO$, m. p. 195°; $SnCl_4,2(p)OH{\cdot}C_6H_4{\cdot}CHO$, m. p. 185°; $SnCl_4,2(p)OMe{\cdot}C_6H_4{\cdot}CHO$, m. p. 158°; $SnCl_4,2COPhMe$, m. p. 131—133°; $SnCl_4,2Ph{\cdot}CO_2Et$, m. p. 40°; $SnCl_4,2(p)C_6H_4Me{\cdot}CO_2Et$; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CO_2Et$, m. p. 134°; $SnBr_4,2(o)OH{\cdot}C_6H_4{\cdot}CO_2Me,2H_2O$, m. p. 67—68°; $SnCl_4,2Ph{\cdot}CO_2H$, m. p. about 90°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CO_2H$, m. p. 85—112°; $SnCl_4,2Ph{\cdot}CO{\cdot}NH_2$, m. p. about 227°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CO{\cdot}NH_2$, m. p. 238—239°; $SnCl_4,2(o)OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, m. p. 205°; and also the following, which are yellow or yellowish: $SnCl_4,2C_4OH_3{\cdot}CHO$, unstable; $SnBr_4,2(p)OH{\cdot}C_6H_4{\cdot}CHO$, m. p. 154°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}COMe$, m. p. 120°. All these compounds are decomposed by water, and contain 1 molecule of the inorganic to 2 of the organic component. Their composition may be represented, therefore, by the general expression $SnX_4,2R{\cdot}CO{\cdot}A$, where X is chlorine or bromine, R is Ph, $\cdot C_6H_4{\cdot}OH$, $\cdot C_6H_4{\cdot}OMe$, $\cdot CHPh{:}CH$, or $\cdot C_4OH_3$, and A is H, Me,

OH, OEt, or NH_2. The common constituent of all these compounds is the carbonyl group, which therefore is the means by which the organic and the inorganic components are linked. The co-ordination number of tin is six. Moreover, additive compounds of the tin series are formed, almost without exception, extra-molecularly, not intra-molecularly. Therefore the two organic molecules of the additive compound probably occupy the two free co-ordination positions of the SnX_4 molecule, being linked by the oxygen, since tin has a much greater affinity for oxygen than for carbon. These views lead to the constitution $X_4Sn\begin{matrix}\leftarrow O{:}CRA\\ \leftarrow O{:}CRA\end{matrix}$ for the preceding additive compounds.

These views, in conjunction with Thiele's theory, are utilised by the author to explain the facts that in a compound containing an unsaturated group the saturation of this group tends to diminish the colour intensity, whilst by the formation of a molecular additive compound colour is produced or intensified. For example, a substance, $\begin{matrix}R\\ R\end{matrix}\!\!>\!\!C{:}O$, in virtue of the residual affinities of the carbon and oxygen atoms, is converted by the addition of Y·Y into a more saturated system, $\begin{matrix}R\\ R\end{matrix}\!\!>\!\!CY{\cdot}OY$, with a corresponding diminution or loss of colour; this is not surprising, because, according to modern views, the colour of purely organic substances is due primarily to the presence of unsaturated groups. When, however, an extramolecular additive compound, such as those above, is formed by a neutralisation of the residual affinity of the oxygen atom only, the unsaturated carbon atom acquires a more pronounced unsaturated character, approximating to that of tervalent carbon, and therefore may be regarded as a specific chromophore, and the additive compound, under suitable circumstances, may be coloured or exhibit halochromy.

In the author's opinion the action of catalysts in hydrolysis, esterification, ketone-synthesis, etc., may be explained by the initial formation of a molecular compound of the catalyst and the organic substance at its carbonyl oxygen atom. C. S.

Action of Chloride of Sulphur and of Sulphuryl Chloride on Piperonal. Karl Weisse (*Ber.*, 1910, 43, 2605—2606. Compare D.R.-P. 165727).—Piperonal reacts to only a slight extent when distilled with sulphuryl chloride, but when a mixture of the two compounds is kept at the ordinary temperature for two days a good yield of *chloropiperonal*, $C_8H_5O_3Cl$, is obtained; it crystallises from alcohol in brilliant needles, m. p. 114—115°.

When this chloro-derivative is heated with chloride of sulphur at 150° for an hour, and then at 130° for three hours, a resinous product is obtained, which loses carbon dioxide when heated, forming *chloroprotocatechualdehyde*, $C_7H_5O_3Cl$, m. p. 211°.

Chloroprotocatechualdehyde reacts with an alcoholic potassium hydroxide solution of ethyl chlorocarbonate, yielding the *ethyl carbonate* derivative, $C_{10}H_9O_5Cl$, which crystallises from water in glistening plates, m. p. 135°. J. J. S.

Condensation Products of *o*-Phthalaldehyde. III. Johannes Thiele and Ernst Weitz (*Annalen*, 1910, 377, 1—22. Compare Thiele and Falk, Abstr., 1906, i, 750; Thiele and Schneider, Abstr., 1909, i, 929).—Ketones with the grouping $CH_3{\cdot}CO{\cdot}CH_2$ can react with *o*-phthalaldehyde in two distinct ways: (*a*) formation of a hydrindone derivative, as in the case of acetone or acetophenone; (*b*) formation of a benzo*cyclo*heptadienone, as in the case of diethyl ketone.

It is shown that methyl ketones which contain a normal carbon chain react according to the latter scheme; thus methyl ethyl, methyl propyl, and methyl *n*-butyl ketones yield respectively methyl-, ethyl-, and propyl-benzo*cyclo*heptadienones, $C_6H_4{<}^{CH:CR}_{CH:CH}{>}CO$. Naphthalene derivatives do not appear to be formed, but small amounts of acylhydrindones can be detected among the condensation products. Methyl *iso*butyl ketone yields as chief condensation product *iso*valerylhydrindone, and practically no *iso*propylbenzo*cyclo*heptadienone. Methyl *iso*propyl ketone yields isobutyrylhydrindone, as there is no methylene group present capable of yielding a benzo*cyclo*heptadienone derivative.

Phthalaldehyde also condenses readily with nitromethane, yielding nitrohydrindone, which reacts in the enolic form, nitrohydroxyhydrindene, as it yields an acetyl derivative and a methyl ether. Its constitution has been determined by conversion into Gabriel's aminohydrindone.

*Benzo*cyclo*heptadienone*, $C_6H_4{<}^{CH:CH}_{CH:CH}{>}CO$, prepared by heating the carboxylic acid (Abstr., 1909, i, 930) with 0·5% hydrochloric acid at 200° for four to five hours, crystallises from light petroleum in pale yellow plates, m. p. 66—67°, and does not react with phenylhydrazine or hydroxylamine. The *dibromide*, $C_{11}H_{18}OBr_2$, forms colourless needles, m. p. 204°. *Dimethylbenzo*cyclo*heptadienone*,

$$C_6H_4{<}^{CH:CMe}_{CH:CMe}{>}CO,$$

prepared from diethyl ketone and phthalaldehyde in the presence of methyl-alcoholic potassium hydroxide solution, crystallises from dilute alcohol in colourless plates, m. p. 85°; *diphenylbenzo*cyclo*heptadienone*, $C_{23}H_{16}O$, obtained when dibenzyl ketone is used, crystallises in pale yellow prisms, m. p. 118·5°, and does not yield a dibromide; *methylbenzo*cyclo*heptadienone*, $C_{12}H_{10}O$, crystallises from light petroleum (40—70°) in felted needles, m. p. 61°; the corresponding *ethyl* derivative, $C_{13}H_{12}O$, has m. p. 42—43°, and the n-*propyl* derivative, $C_{14}H_{14}O$, has b. p. 188°/13 mm., and solidifies when kept in a freezing mixture.

*Diphenylbenzo*cyclo*heptanone*, $C_6H_4{<}^{CH_2{\cdot}CHPh}_{CH_2{\cdot}CHPh}{>}CO$, prepared by reducing the corresponding dienone with sodium amalgam and alcohol in the presence of acetic acid, crystallises from 75% alcohol in colourless needles, m. p. 158°. The ketone does not react with phenylhydrazine or semicarbazide, but with magnesium methyl iodide yields *diphenylmethylbenzo*cyclo*heptanol*, $C_6H_4{<}^{CH_2{\cdot}CHPh}_{CH_2{\cdot}CHPh}{>}CMe{\cdot}OH$, which

forms colourless crystals, m. p. 211°, and is stable towards permanganate.

Dimethylbenzocycloheptanol, $C_6H_4<\begin{matrix}CH_2\cdot CHMe\\CH_2\cdot CHMe\end{matrix}>CH\cdot OH$, obtained by reducing the corresponding dienone, crystallises from dilute alcohol in colourless needles, m. p. 123—124°, and yields an *acetyl* derivative, m. p. 141°. *Diphenylbenzocycloheptanol*, $C_{23}H_{22}O$, forms colourless plates, m. p. 160°. *Benzocycloheptanol*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot OH$, prepared from benzo*cyclo*heptadienone, has m. p. about 80°.

iso*Valerylhydrindone* (1-*hydroxy*-2-iso*valerylhydrindene*),

$$C_6H_4<\begin{matrix}C(OH)\\-CH_2-\end{matrix}>C\cdot CO\cdot CH_2\cdot CMe_2,$$

crystallises from methyl alcohol in needles, soluble in alkalis, and gives a red to reddish-violet coloration with ferric chloride. When a small amount of alkali is used in the condensation, much phenylnaphthylene ketone is formed. iso*Butyrylhydrindone* (1-*hydroxy*-2-iso*butyrylhydrindene*), $C_6H_4<\begin{matrix}C(OH)\\-CH_2-\end{matrix}>C\cdot CO\cdot CHMe_2$, has b. p. 170—174°/13—14 mm., and m. p. 35—36°.

2-*Nitro*-1-*hydrindone* (2-*nitroindenol*), $C_6H_4<\begin{matrix}C(OH)\\-CH_2-\end{matrix}>C\cdot NO_2$, crystallises from light petroleum (100°) in slender, sulphur-yellow needles, m. p. about 117° (decomp.). It dissolves in alkali hydroxide solutions and is decomposed when boiled with water. The *acetyl* derivative, $C_{11}H_9O_4N$, crystallises in slender, yellow needles, turns dark coloured at 108—109°, melts and decomposes above 120°, and yields a *dibromide*, $C_{11}H_9O_4NBr_2$, in the form of colourless, compact crystals, m. p. 136°. The *methyl ether* of the nitro-derivative, $C_9H_9O_3N$, is obtained readily from the acetyl derivative by the action of methyl alcohol and hydrogen chloride; it crystallises in pale yellow plates, m. p. 83°.

Hydrobenzoin-o-dialdehyde, $CHO\cdot C_6H_4\cdot CH(OH)\cdot CH(OH)\cdot C_6H_4\cdot CHO$, prepared by reducing phthalaldehyde with zinc dust in the presence of alcohol and glacial acetic acid at the ordinary temperature, crystallises from alcohol in minute needles, m. p. 176—177°. Its solution in concentrated sulphuric acid has an intense yellow colour with a greenish-yellow fluorescence. Its *phenylhydrazone*, $C_{28}H_{26}O_2N_4$, crystallises from aniline, and has m. p. above 260°. When oxidised with nitric acid the dialdehyde yields hydrodiphthalyl (compare Hasselbach, Abstr., 1888, 485), but with alkaline permanganate yields benzil-*o*-dicarboxylic acid (Graebe, Abstr., 1888, 1095; 1890, 989). Concentrated sulphuric acid reacts with a solution of the dialdehyde in glacial acetic acid, yielding 2-o-*aldehydophenyl*-3-*indone*, $C_6H_4<\begin{matrix}CO\\CH\end{matrix}>C\cdot C_6H_4\cdot CHO$, which crystallises from alcohol in brilliant, orange-red needles, m. p. 141°. An amorphous by-product is formed at the same time, and the amount of this increases if the reaction mixture is heated for some time. The indone derivative reduces ammoniacal silver nitrate solution and also alkaline permanganate, and yields a *dibromide*, $C_{16}H_{10}O_2Br_2$, m. p. above 240°. A small amount of this indone is formed in the preparation of phthaldehyde. J. J. S.

Synthesis of Ketones in the Tetrahydroaromatic Series. Georges Darzens and H. Rost (*Compt. rend.*, 1910, **151**, 758—759). —This paper contains an account of further applications of the general reaction already described (this vol., i, 322) to *cyclo*hexene. By treating this hydrocarbon with *n*-butyryl chloride in presence of aluminium chloride, a condensation product is obtained, which loses hydrogen chloride when heated with diethylamine, forming n-*butyryl*cyclo*hexene*, $C_3H_7\cdot CO\cdot C_6H_9$, b. p. 225—226°, 113—114°/7 mm.; the *semicarbazone* has m. p. 171°. iso*Valeryl*cyclo*hexene* has b. p. 233°, 128—130°/7 mm.; the *semicarbazone* has m. p. 180°. *Heptoyl*cyclo*hexene* has b. p. 274—275°, 140—141°/5 mm.; the *semicarbazone* has m. p. 145°. *Laurylcyclohexene*, b. p. 342—343°, 209—211°/6 mm., forms a *semicarbazone*, m. p. 125°.

The foregoing ketones may be utilised for the production of hexahydroaromatic ketones, the reduction being effected by catalytic hydrogenation in presence of reduced nickel.

By condensing tetrahydroacetophenone with ethyl chloroacetate in presence of sodium ethoxide, *ethyl methylcyclohexenylglycidate*, $O<\begin{matrix}CMe\cdot C_6H_9\\ CH\cdot CO_2Et\end{matrix}$, has been obtained. This substance has b. p. 145—148°/14 mm., and on hydrolysis gives an unstable acid, which loses carbon dioxide when heated in a vacuum, forming *tetrahydroatropaldehyde*, $C_6H_9\cdot CHMe\cdot CHO$, b. p. 90—93°/15 mm. W. O. W.

The Pinacone Transformation in the Case of Cyclic Compounds. I. Hans Meerwein and Walter Unkel (*Annalen*, 1910, **376**, 152—163).—1-*iso*Propyl*cyclo*pentane-1 : α-diol,

$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CMe_2\cdot OH,$$

prepared by the action of magnesium methyl iodide on methyl α-hydroxy*cyclo*pentanecarboxylate, readily undergoes the pinacone transformation when heated with dilute sulphuric or oxalic acid. An intermediate product is probably the oxide, $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CMe_2\\ O\end{matrix}$, but the final product isolated is 1 : 1-dimethyl*cyclo*hexan-6-one, the constitution of which was determined by oxidation to αα-dimethyladipic acid by means of nitric acid. The reaction (cyclic pinacone transformation) consists in the conversion of a 5-carbon into a 6-carbon ring, and is of interest as bearing on certain transformations in the terpene series.

Reactions of the same type are the conversion of pulegenic acid (*iso*propylidenemethyl*cyclo*pentanecarboxylic acid) into pulenone (1 : 4 : 4-trimethyl*cyclo*hexan-5-one) (compare Wallach, Abstr., 1904, i, 74); also the conversion of di*cyclo*pentanepinacone into 1 : 1-tetramethylene*cyclo*hexan-2-one (Meiser, Abstr., 1899, i, 742), and the transformation of fluorenone into a phenanthrene derivative when reduced with zinc and acetyl chloride, a pinacone being the intermediate product, which has not been isolated:

$$\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CO \longrightarrow \begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix} \longrightarrow \begin{matrix}C_6H_4\cdot CO\\ C_6H_4\cdot C\end{matrix}<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}$$

(compare Klinger and Lonnes, Abstr., 1896, i, 691).

Methyl cyclo*pentan*-1-*ol*-1-*carboxylate*, $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CO_2Me$, is readily prepared from the acid (Gärtner, Abstr., 1893, i, 557) by the usual method. It has b. p. 87°/23 mm., or 84°/16 mm. 1-iso*Propyl*-cyclo*pentane*-1 : *α-diol*, $C_8H_{16}O_2$, crystallises from light petroleum in glistening, colourless prisms, m. p. 62°, and b. p. 105—110°/15 mm. 1 : 1-*Dimethyl*cyclo*hexan*-6-*one*, $CH_2<\begin{matrix}CH_2—CO\\ CH_2\cdot CH_2\end{matrix}>CMe_2$, is a colourless oil, and yields a *semicarbazone*, $C_9H_{17}ON_3$, which crystallises in large, flat needles, m. p. 196—197°. The pure ketone, prepared by hydrolysing the semicarbazone with 10% sulphuric acid, has b. p. 59·5°/14 mm. or 170·2—170·4°/758 mm., D^{20} 0·9194, and n_D^{20} 1·44744, and has an odour of camphor and menthone.

A small amount of an unsaturated hydrocarbon accompanies the crude ketone. J. J. S.

Reaction between Organic Magnesium Compounds and Unsaturated Compounds Containing Alkyloxy-groups. Grace Potter Reynolds (*Amer. Chem. J.*, 1910, **44**, 305—331).—The reactions between organic magnesium compounds and unsaturated compounds have been studied by Kohler (Abstr., 1905, i, 208; 1907, i, 139, 1050) with special reference to the effect of hydrocarbon residues in substances containing the chain C:C·C:O, as the result of which it is possible to predict the mode of addition of a magnesium compound to such a substance. It has also been shown that in the reactions with ethyl α-cyanocinnamate (Abstr., 1905, i, 347) and ethyl benzylidenemalonate (Abstr., 1905, i, 700) the presence of the cyano- and carbethoxy-groups in the α-position prevents the replacement of the alkyloxy-group, and therefore only αδ-additive products are obtained. In continuation of this work, an investigation has been made of the influence of alkyloxy-groups on the mode of addition. An attempt has been made to use the Grignard reagent for the study of keto-enol-tautomerism, but it has been found to be unsuitable for the purpose.

Magnesium methyl iodide reacts instantaneously with phenyl formylethyl ketone when dissolved in ethyl ether, but does not react with it in an amyl ether solution, and it is therefore evident that the method cannot be used for the estimation of the hydroxyl group in this ketone (compare Hibbert and Sudborough, Trans., 1904, **85**, 933, and Zerewitinoff, Abstr., 1907, ii, 509).

Ethyl hydroxymethylenemalonate and phenyl formylethyl ketone were selected for the experiments to ascertain whether the nature of the products obtained in the Grignard reaction can serve for the estimation of the relative amounts of ketonic and enolic modifications. Magnesium phenyl bromide reacts with ethyl hydroxymethylenemalonate to form a product, which, when decomposed in the usual way, yields ethyl benzylidenemalonate. Magnesium ethyl bromide also reacts with ethyl hydroxymethylenemalonate, but the product could not be identified.

Ethyl α-phenylpropylmalonate, $CHPhEt\cdot CH(CO_2Et)_2$, b. p. 187—188°/22 mm., prepared by the action of magnesium ethyl bromide on ethyl benzylidenemalonate, is a colourless liquid; the corresponding *acid*, m. p. 74°, crystallises with $1H_2O$.

Magnesium phenyl bromide reacts with phenyl formylethyl ketone to form a product which yields benzylidenepropiophenone. With magnesium ethyl bromide a substance was obtained consisting of impure phenyl α-methylbutenyl ketone, which was identified by means of its *dibromide*, m. p. 67°, and also by its conversion into phenyl β-phenyl-α-methylbutyl ketone by the action of magnesium phenyl bromide. *Phenyl β-phenyl-α-methylbutyl ketone*,

$$CHPhEt\cdot CHMe\cdot COPh,$$

m. p. 60·5°, prepared by the action of magnesium ethyl bromide on benzylidenepropiophenone, forms white, slender needles; its *oxime* has m. p. 119°.

Ethyl ethoxymethylenemalonate reacts with magnesium phenyl bromide with formation of a product which yields ethyl diphenylmethylmalonate; on treating this ester with alcoholic potassium hydroxide, *potassium ethyl diphenylmethylmalonate* is obtained. When ethyl ethoxymethylenemalonate is treated with magnesium ethyl bromide, *ethyl α-ethylpropylmalonate*, $CHEt_2\cdot CH(CO_2Et)_2$, b. p. 138°/21 mm., is obtained as a colourless, mobile liquid.

β-Ethoxypropiophenone reacts with magnesium phenyl bromide with formation of *diphenylethoxyethylcarbinol*,

$$OEt\cdot CH_2\cdot CH_2\cdot CPh_2\cdot OH,$$

b. p. 207°/21 mm., m. p. 78°, which crystallises in white plates. This ketone also reacts with magnesium ethyl bromide with production of *phenylethylethoxyethylcarbinol*, $OEt\cdot CH_2\cdot CH_2\cdot CPhEt\cdot OH$, b. p. 151°/24 mm., as a colourless, mobile liquid.

Phenyl β-ethoxystyryl ketone can be obtained in fair yield by boiling phenyl dibromostyryl ketone with sodium ethoxide. This ketone reacts with magnesium ethyl bromide in presence of the usual quantity of ether to form a product, which, when decomposed with hydrochloric acid at 0°, yielded ethoxydiphenylethylallyl alcohol, together with ethoxyphenylethylpropiophenone and two solid *compounds*, $C_{34}H_{32}O_3$, one of which has m. p. 205° and forms white needles, whilst the other has m. p. 185° and forms yellow needles; the white substance slowly changes in solution into the yellow compound. *Ethoxydiphenylethylallyl alcohol*,

$$OEt\cdot CPh{:}CH\cdot CPhEt\cdot OH,$$

m. p. 60·5°, crystallises in white, slender needles. *Ethoxyphenylethylpropiophenone*, $OEt\cdot CPhEt\cdot CH_2\cdot COPh$, b. p. 96°/18 mm., is a colourless, mobile liquid; its *semicarbazide-semicarbazone* has m. p. 161°. In another experiment on the action of magnesium ethyl bromide on phenyl β-ethoxystyryl ketone, a much larger quantity of ether was used, and, on decomposing the product, the same three solid compounds were obtained, together with *γε-diphenyl-*$\Delta^{\beta\delta}$*-heptadiene*, $CPhEt{:}CH\cdot CPh{:}CHMe$, b. p. 191—195°/20 mm., as a colourless liquid. When phenyl β-ethoxystyryl ketone is added to magnesium phenyl bromide in presence of a large quantity of ether, and the product is decomposed in the usual way, tetraphenylallyl alcohol is

obtained, but if the reaction is carried out in presence of only the usual quantity of ether, *ethoxytriphenylallyl alcohol*,

$$OEt\cdot CPh{:}CH\cdot CPh_2\cdot OH,$$

m. p. 120·5°, is produced, which crystallises in white, slender needles.

These experiments with phenyl β-ethoxystyryl ketone show that in the reaction between organic magnesium compounds and unsaturated compounds having an alkyloxy-group in the β-position, either αβ- or αδ-addition takes place, and the alkyloxy-group of the resulting substance may or may not be replaced subsequently by a hydrocarbon residue. It is also shown that the influence of the β-ethoxy-group on the mode of addition is approximately the same as that of the phenyl group. E. G.

Action of Light on Unsaturated Ketones in Presence of Uranyl Salts. Paul Praetorius and Franz Korn (*Ber.*, 1910, **43**, 2744—2746).—Distyryl ketone, when exposed to the action of light in presence of uranyl chloride in acetic acid suspension, yields a colourless compound, $(C_{17}H_{14}O)_2$, m. p. 245° (decomp.), crystallising in needles. On oxidation with chromic acid, α-truxillic acid, benzoic acid, and carbon dioxide are formed. Accordingly, the formula

$$CHPh{:}CH\cdot CO\cdot CH<\begin{matrix}CHPh\\CHPh\end{matrix}>CH\cdot CO\cdot CH{:}CHPh$$

is assigned to the bimolecular compound.

A by-product is a substance soluble in acetic acid, which crystallises in colourless needles, m. p. 183°.

The red di-*p*-methoxydistyryl ketone uranyl chloride is stable towards light.

Dibenzylidene*cyclo*pentanone uranyl chloride is decomposed to a colourless compound, crystallising in pointed prisms, m. p. 248°, which gives an orange-yellow coloration with concentrated sulphuric acid. E. F. A.

Existence of 2 : 2′-Dinitrobenzoin. Thor Ekecrantz and Alfr. Ahlqvist (*Ber.*, 1910, **43**, 2606—2609. Compare Abstr., 1908, i, 347; Popovici, Abstr., 1907, i, 628).—A modification of Popovici's method (Abstr., 1908, i, 550) for the preparation of the so-called 2 : 2′-dinitrobenzoin is described, and the yield is increased to 0·4 gram from 25 grams of aldehyde. The product melts at 168—169° (corr.), not 161—162°, contains two atoms of hydrogen more than the benzoin, and is not oxidised to any appreciable extent by chromic acid mixture. J. J. S.

Colour and Affinity for Mordants of Anthraquinone Derivatives. II. Gustav Heller (*Ber.*, 1910, **43**, 2890—2892. Compare Abstr., 1908, i, 995).—According to previous workers, the salts of anthraquinone-2 : 3-dicarboxylic acid, as well as those of the 1 : 3- and 1 : 4-acids, are reddish (compare Elbs and Eurich, Abstr., 1890, i, 511). Since this does not agree with the view put forward in the former paper, the author has prepared these substances, and finds that their alkaline solutions are colourless when pure. Nevertheless, they are fixed to a certain extent by some metallic hydroxides.

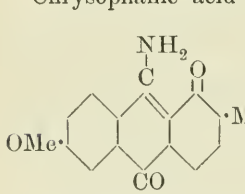
[With Erich Grünthal.]—*o*-Xyloyl-*o*-benzoic acid, prepared by the Friedel and Crafts' reaction according to the method previously described (Abstr., 1908, i, 994), has m. p. 167° (F. Meyer, Abstr., 1882, 848, gave 161·5°).

2 : 3-Dimethylanthraquinone has m. p. 205—206° (Elbs and Eurich gave 183°; Limpricht, Abstr., 1900, i, 599, gave 200°).

1 : 4-Dimethylanthraquinone has m. p. 140—141° (Elbs and Eurich gave 118—119°). R. V. S.

Chrysophanic Acid. Otto A. Oesterle and U. Johann (*Arch. Pharm.*, 1910, **248**, 492—500).—The dimethyl ether, obtained together with a little monomethyl ether by treating chrysophanic acid with methyl sulphate, is partly demethylated by concentrated sulphuric acid on the water-bath or by aluminium chloride at 115°, yielding only one methyl ether, identical with the above. Consequently the hydroxyl groups in chrysophanic acid are not methylated with equal ease; the one which is easily methylated occupies probably a β-position, the other an α-position. Ethyl chloroacetate is a reagent which readily attacks hydroxyl groups in the α-position (D.R.-P. 158277); its action on chrysophanic acid, however, does not lead to definite results; the authors claim from them, however, that one hydroxyl group is probably in a β-position.

Chrysophanic acid methyl ether and aqueous ammonia, at 140°, yield a *substance*, $C_{16}H_{13}O_3N,\frac{1}{2}H_2O$, m. p. 237—239°, which crystallises in brownish-red needles, and has the composition of an amino-chrysophanic acid methyl ether; it is converted by nitrous acid into chrysophanic acid methyl ether, a reaction which is explained, in accordance with Scholl and Parthey's results (Abstr., 1906, i, 439), by ascribing to the substance the annexed constitution, assuming that the hydroxyl groups in chrysophanic acid are in positions 1 and 6 and the methyl group in position 2. C. S.



So-called Methylchrysophanic Acid. Otto A. Oesterle and U. Johann (*Arch. Pharm.*, 1910, **248**, 476—491).—Chrysophanic acid, when prepared from rhubarb or chrysarobin, is accompanied by a substance containing methoxyl, which is stated by Hesse to be methyl-chrysophanic acid (Abstr., 1900, i, 41). Gilson claims that in the case of chrysophanic acid from rhubarb the accompanying substance is rheochrysidin (*Arch. internat. Pharm. Thér.*, 1905, **14**, 492). The authors show, however, that in chrysophanic acid from both sources the accompanying substance is the methyl ether of frangula-emodin. Chrysophanic acid, obtained by the oxidation of chrysarobin in alkaline solution, is methylated in the manner described previously (Abstr., 1905, i, 911), and the yellow substance, m. p. 224°, accompanying the dimethyl ether is separated therefrom by dilute alcohol; it has after repeated recrystallisation m. p. 226—227° and the composition of a trimethoxymethylanthraquinone. It can be demethylated by aluminium chloride at 115°, or, better, by concentrated sulphuric acid at 160°,

yielding a substance, m. p. 256—257°, identical with frangula-emodin (Abstr., 1908, i, 350), the identity being confirmed by a comparison of the *triacetates*, $C_{14}H_4O_2Me(OAc)_3$, yellow needles, m. p. 197—198°. Hence, the substance accompanying chrysophanic acid, obtained from chrysarobin, is a methyl ether of emodin. It can be isolated, although with considerable difficulty, by extracting the acetylated acid with alcohol at 50—55°; the acetate of emodin methyl ether thus obtained has m. p. 181—183°, but it still contains a little acetate of chrysophanic acid, because after hydrolysis, recrystallisation of the hydrolysed product, and re-acetylation, the m. p. is 190—191·5°. The hydrolysis of the acetate by aqueous potassium hydroxide yields an *emodin methyl ether*, $C_{14}H_4O_2Me(OH)_2\cdot OMe$, orange-red needles, m. p. 206—207°, identical with that obtained by the partial demethylation of frangula-emodin trimethyl ether by aluminium chloride at 115° for three-quarters of an hour. The ether dissolves in dilute alkali hydroxides with an intense red colour, and forms a *dipropionate*, m. p. 162—164°. It is shown to be identical with Gilson's rheochrysidin by its crystallographic properties, and with Hesse's physcion (lichen-chrysophanic acid) (Abstr., 1906, i, 280) by a comparison of the *dibenzoates*, m. p. 230°, and of the products of reduction by zinc and acetic acid. C. S.

Some Derivatives of Acenaphthenequinone. M. Zsuffa (*Ber.*, 1910, **43**, 2915—2922).—Naphthalic anhydride does not enter into the Friedel and Crafts' reaction with aromatic hydrocarbons, so that the carbonyl groups in the 1 : 8-position behave differently from those in the 1 : 2-position, as in phthalic anhydride. Acenaphthenequinone, $C_{10}H_6<\begin{matrix}CO\\|\\CO\end{matrix}$, however, readily undergoes this and other condensations. With aromatic hydrocarbons or with chlorobenzene, diaryl derivatives of the type $C_{10}H_6<\begin{matrix}CAr_2\\|\\CO\end{matrix}$ are produced, and these are even more readily obtained from dichloroacenaphthenone, $C_{10}H_6<\begin{matrix}CCl_2\\|\\CO\end{matrix}$. Acenaphthenequinone also condenses in a similar manner with dimethylaniline in the presence of zinc chloride or of concentrated hydrochloric acid, and with phenols (resorcinol) in presence of zinc chloride or tin chloride. From 9 : 9-diphenylacenaphthenone, diphenyl-α-naphthylmethane can be prepared with good yield, whilst from 9 : 9-tetramethyldiaminodiphenylacenaphthenone the corresponding hydrocarbon can also be prepared. The latter is readily oxidised to the naphthyl analogue of malachite-green.

9 : 9-Diphenylacenaphthenone (Beschke, Abstr., 1909, i, 918) can be obtained from acenaphthenequinone, or, better (yield almost quantitative), from dichloroacenaphthenone. In the latter case the action is vigorous, and should be moderated by the use of a solvent (carbon disulphide). When the substance is heated with alcoholic potassium hydroxide for four hours on the water-bath, *8-diphenylmethyl-1-naphthoic acid*, $C_{24}H_{18}O_2$, crystallising in small, colourless laminæ, m. p. 227°, is obtained. On distillation in a vacuum with two and a-half times its weight of barium hydroxide, this yields *diphenyl-α-naphthylmethane*,

$C_{10}H_7\cdot CHPh_2$, which forms colourless needles, m. p. 150°. 8-Diphenylmethyl-1-naphthoic acid, when oxidised with chromic acid, gives *diphenylnaphthalide*, $C_{10}H_6<^{CPh_2}_{CO-}>O$, which crystallises in colourless needles, m. p. 204°.

9 : 9-*Dichlorodiphenylacenaphthenone*, $C_{24}H_{14}OCl_2$ (from dichloroacenaphthenone and chlorobenzene), forms small, colourless needles, m. p. 151°. 8-*Dichlorodiphenylmethyl*-1-*naphthoic acid*, $C_{24}H_{16}O_2Cl_2$, crystallises in small, colourless laminæ, m. p. 224—225°.

9 : 9-*Tetramethyldiaminodiphenylacenaphthenone*, $C_{28}H_{26}ON_2$, is prepared by heating acenaphthenequinone with dimethylaniline and a small quantity of concentrated hydrochloric acid to 150° for three hours. It forms small, yellow laminæ or needles, m. p. 204—205°. Its solution in glacial acetic acid is coloured malachite-green by oxidising agents, but the coloration disappears on dilution with water. Prolonged boiling with alcoholic potassium hydroxide leaves the compound unaffected. The *hydrochloride*, $C_{28}H_{26}ON_2,2HCl$, prepared with hydrogen chloride in benzene solution, forms colourless needles, which with water regenerate the base. The *picrate*,

$$C_{28}H_{26}ON_2,2C_6H_3O_7N_3,$$

forms lemon-yellow crystals. The *dimethiodide*, $C_{28}H_{26}ON_2,2MeI$, has m. p. 224—225° (decomp.). When 9 : 9-tetramethyldiaminodiphenylacenaphthenone is boiled for four hours with amyl-alcoholic potassium hydroxide, 8-*tetramethyldiaminodiphenylmethyl*-1-*naphthoic acid*, $C_{28}H_{28}O_2N_2$, is obtained. It crystallises in pale yellow needles, m. p. 260—262°, and is soluble in acids and alkalis. The *barium* salt is sparingly soluble in water. Distillation of the acid with barium hydroxide yields *tetramethyldiaminodiphenyl-α-naphthylmethane*, $C_{10}H_7\cdot CH(C_6H_4\cdot NMe_2)_2$, which forms yellow needles, m. p. 161—162°, and on oxidation gives *naphthyl-malachite-green*.

Anhydrodiresorcinolacenaphthenone, $^{C_{10}H_6}_{CO-}>C<^{C_6H_3\cdot OH}_{C_6H_3\cdot OH}>O$, is prepared by heating acenaphthenequinone with resorcinol and zinc chloride for two hours at 180°. It is a pale brown, amorphous powder, which is soluble in alkali hydroxides, giving a yellowish-red coloration and a green fluorescence. R. V. S.

Derivatives of the Dextro-Antipode of Natural *l*-Menthol. Leo A. Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 714—718. Compare Skwortzoff, *ibid.*, 1910, 42, 55).—The oil of Bucco leaves, freed from diosphenol by repeated treatment with 20% alkali hydroxide, was dried and fractionated. The fraction boiling at 190—225° was reduced with sodium and alcohol, the product distilled in steam, and the distillate then extracted with ether, dried, and redistilled. The fraction boiling at 200—220°, containing most of the menthol, was then converted into sodium menthylxanthate, which, by the action of iodine, was converted to the *disulphide*, thus :

$$C_{10}H_{19}O\cdot CS_2Na + 2I = S_2(CS\cdot O\cdot C_{10}H_{19})_2 + 2NaI,$$

m. p. 92—92·5°, $[\alpha]_C$ +183·4°, $[\alpha]_D$ +226·3°.

The latter with potassium cyanide gave the *anhydride*, $(C_{10}H_{19}O\cdot CS)_2S$, m. p. 147·5—148°, forming yellowish-green, hexagonal crystals.

In toluene solution at 20° it gave $[\alpha]_D$ +46·42°, +46·50°, $[\alpha]_E$ +21·17°, the corresponding *l*-menthylxanthic anhydride giving $[\alpha]_D$ −46·50°, $[\alpha]_E$ −21·30°. The new compound must therefore be a derivative of *d*-menthol, and the two substances are optical antipodes. The disulphide of *l*-menthol has $[\alpha]_D$ −182·8°, $[\alpha]_D$ −225·1°. By saponification the *d*-menthylxanthic anhydride yields a menthol, m. p. 42°. Z. K.

Constitution of Fenchone. V. and VI. Louis Bouveault and F. Levallois (*Bull. Soc. chim.*, 1910, [iv], 7, 963—968, 968—973).—These two papers are in continuation of work published previously (this vol., i, 686), and record results given already in part (Abstr., 1909, i, 497, 595). Fuller experimental details and an outline of the principles underlying the syntheses effected are now given.

The following results are new. *apo*Fenchene hydrochloride (Abstr., 1908, i, 193), treated in succession with magnesium ethyl bromide and carbon dioxide, furnishes an acid having the same boiling point as dihydrofencholenic acid, but yielding an anhydride having b. p. 202°/20 mm., which is 3° lower than that of the expected anhydride (this vol., i, 573), and an amide, having m. p. 104°, as against 108° for dihydrofencholenamide, although it forms nacreous leaflets in all respects similar to those formed by the latter. T. A. H.

Action of Magnesium on a Mixture of Allyl Bromide and Pulegone (Synthesis of 1-Methyl-3-allyl-4-*iso*propylidene*cyclo*hexan-3-ol). G. G. von Fersen (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 681—683).—1-*Methyl*-3-*allyl*-4-iso*propylidene*cyclo*hexan*-3-*ol*,

$$\begin{array}{l} CHMe\cdot CH_2\cdot C(C_3H_5)\cdot OH \\ | \qquad\qquad\qquad\quad | \\ CH_2\text{—}\cdot CH_2\cdot C{:}CMe_2 \end{array},$$

obtained when magnesium is treated with a small quantity of allyl bromide and a mixture of pulegone and allyl bromide then added drop by drop, has b. p. 135—135·5°/27 mm., $D_4^{21\cdot95}$ 0·9264, n_D 1·49039; it is a colourless liquid with a pleasant odour, which on oxidation with permanganate yields a complex mixture of acid and neutral products. Z. K.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. II. α-Pinene-*o*-hydroxylamineoxime. Guido Cusmano (*Gazzetta*, 1910, 40, ii, 122—131. Compare this vol., i, 685).—From α-pinene bisnitrosochloride, the author has prepared α-pinene-*o*-hydroxylamineoxime similarly to the *d*-limonene-*o* hydroxylamineoxime previously described (*loc. cit.*), but he has found that the compound reacts like the ordinary *m*-hydroxylamineoximes, so that the anomalous behaviour of the *d*-limonene derivative still requires explanation.

α-*Pinene*-o-*hydroxylamineoxime* forms lustrous needles, which decompose about 140°. It reduces Fehling's solution in the cold, and is soluble in alkalis, whilst with acids it yields monobasic salts. The *hydrochloride*, $C_{10}H_{18}O_2N_2$,HCl, which is formed in addition to the free base in the preparation of the substance, crystallises in tufts of silky needles, m. p. about 170°; when the solvent contains water, it

crystallises in hexagonal laminæ with $1H_2O$, and these sinter at about 100°, decomposing at 165°. The *sulphate*, $C_{10}H_{18}O_2N_2,H_2SO_4$, forms four-sided tablets. By the action of nitrous acid on either of these salts, the *iso*nitroamineoxime is formed (compare this vol., i, 574). The hydroxylamine group of the hydroxylamineoxime reacts with aldehydes. The *pentylidene* derivative,

$$OH\cdot N{:}C_{10}H_{15}\cdot N{<}\overset{CH\cdot C_4H_9}{\underset{O}{|}},$$

forms flat, quadrangular crystals, m. p. 150°. The *benzylidene* derivative, $OH\cdot N{:}C_{10}H_{15}\cdot N{<}\overset{CHPh}{\underset{O}{|}}$, crystallises in hexagonal laminæ, m. p. 167°. The p-*nitrobenzylidene* compound, $C_{17}H_{21}O_4N_3,C_2H_6O$, forms yellow crystals, m. p. 163—165°.

Pinene-*o*-hydroxylamineoxime is decomposed by very dilute oxalic acid, with formation of carvoxime and hydroxydihydrocarvoxime, so that instead of the elimination of the oxamic grouping, the destruction of the piceanic ring is effected. These two substances are formed in all the reactions in which the hydroxylamineoxime reacts in an acid medium, and hence they occur as by-products in its preparation. By the action of alkalis, the hydroxylamineoxime in time loses the oxamic group, hydroxylamine and nitrosopinene being formed.

o-*Nitroso*iso*nitrosopinene*, $C_{10}H_{15}{<}\overset{NO}{\underset{N\cdot OH}{|}}$, may be obtained by oxidising α-pinene-*o*-hydroxylamineoxime, preferably by dissolving it in dilute sulphuric acid and adding the calculated quantity of potassium dichromate, the dilute solutions being kept cool with ice. It is a crystalline substance, which explodes at about 60°, and readily oxidises in the air, absorbing one atom of oxygen, with production of a yellow *substance*. When a solution of the hydroxylamineoxime hydrochloride is treated with iron alum, a *substance* is obtained containing 5·1% of iron; it is orange-yellow in colour, and decomposes at 110—120°.

R. V. S.

[Essential Oils.] Heinrich Haensel (*Berichte von H. Haensel*, April to September 1910, 6—53).—The flowers of *Gnaphalium avenarium*, used as an insectifuge, yielded 0·04% of dirty green, aromatic oil, which solidified at 4° and had D^{30} 0·921. After treatment with animal charcoal, it was bluish-green in colour, solidified at 7°, had acid number 14·45, ester number 9, and was incompletely soluble in 95% alcohol. The insoluble matter consisted of stearopten, m. p. 48—50°, containing a bluish-green colouring matter. The soluble portion of the oil contained (1) an *acid*, m. p. 34—36°, with an odour recalling that of hexoic acid, (2) *p*-cresol, and (3) an alcohol having a fruity odour.

Syrian peppermint oil (compare this vol., i, 401) gave a terpeneless fraction having the following constants: acid number 1·87, ester number 22·4, acetyl ester number 180 (one hour), corresponding with 6·24% ester menthol and 51·73% free menthol. The crude oil yielded 5% of terpene, having D^{18} 0·8880.

Datura Stramonium leaves yielded 0·045% of a volatile oil of dark brown colour and tobacco-like odour. It had D^{30} 0·9440, solidified at 20°, and after treatment with animal charcoal showed acid number

52·4, and ester number 9·57. The saponified oil contained a minute quantity of an alcohol having a strong odour of tobacco. The aqueous distillate was alkaline and of blue colour, but became colourless on addition of acid, regaining the blue colour on addition of alkali.

Dalmatian yellow sunflowers (Sonnengoldblumen) furnished 0·235% of oil, $D^{18\cdot5}$ 0·9100, $\alpha - 5°10'$, of greenish-yellow colour and pleasant, sweet aroma. It had acid number 8·9 and ester number 87·66, corresponding with 24·12% of alcohol, $C_{16}H_{18}O$. T. A. H.

Spearmint Oil. F. Elze (*Chem. Zeit.*, 1910, 34, 1175).—The carvone-free residue of spearmint oil has an intense spearmint odour, and on distillation under reduced pressure gives the following fractions: b. p. 40—45°/4 mm., 15%, containing 2·8% esters; b. p. 45—75°/4 mm., 15%; b. p. 75—80°/4 mm., 24%, containing 19% esters; b. p. 80—85°/4 mm., 7·5%; and 85—100°/4 mm., 35·0%, containing 31% esters. From the first of these fractions phellandrene was isolated. The last fraction, freed from aldehydes and phenols, furnished on hydrolysis acetic and valeric acids and dihydrocuminyl alcohol. Dihydrocuminyl acetate has the characteristic odour of spearmint oil. T. A. H.

Cold Vulcanisation of Caoutchouc. B. B. Bysoff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 638—647).—A criticism of Weber's theory of the vulcanisation of caoutchouc with sulphur chloride, S_2Cl_2. The chemical explanation of the process is not satisfactory. Regarding caoutchouc as a heterogeneous disperse system consisting of two liquid phases, it will probably have the general properties of a colloid, such, for instance, as the property of adsorption. The change in caoutchouc on vulcanisation with sulphur chloride is due to the adsorption of the latter, the process of vulcanisation is thus physical not chemical. The connexion between the amount of sulphur contained in the caoutchouc after vulcanisation and the concentration of the benzene solutions of sulphur chloride employed has been studied, and the resulting curve, which is hyperbolic, is drawn. Z. K.

Chlorophyll Group. VIII. Formation of Phyllotaonin from Chlorophyllan. Henry K. Malarski and Leon Marchlewski (*Biochem. Zeitsch.*, 1910, 28, 48—52. Compare this vol., i, 692).—When chlorophyllan (15 grams), obtained from stinging nettles, is left for twenty-four hours with 200 c.c. of methyl-alcoholic potassium hydroxide solution, hydrolysis takes place. The mass is poured into 2 litres of water, and the phytol removed by extraction with ether; acetic acid is added, and the ether extraction repeated. The ethereal solution is fractionated by extracting with gradually increasing amounts of hydrochloric acid, namely, from 1 to 20%. The product, soluble in 1% hydrochloric acid, contains chlorophyllanic acid, and the solution in 18% hydrochloric acid gives all the characteristic absorption bands of *allo*phyllotaonin (Kózniewski and Marchlewski, Abstr., 1907, i, 867), and when treated with alkalis gives the absorption bands of phyllotaonin. J. J. S.

Commercial Azolitmin. Paul Scheitz (*Zeit. anal. Chem.*, 1910, 49, 735—736. Compare following abstract).—Azolitmin occurs in commerce in the form of bluish-black scales, contains very little

mineral matter, dissolves in water with a red coloration, but becomes insoluble in water after heating at 100° during three to four hours. It dissolves in ammonia or alkali solutions, forming blue liquids, but is not re-precipitated therefrom by acids, the solutions merely changing colour to red. The substance appears to be an ammonium salt, since it evolves about 8·5% of ammonia on treatment with alkalis.

By dissolving commercial azolitmin in ammonia solution, recovering the colouring matter by adding excess of hydrochloric acid and warming, and then purifying the precipitated product by boiling with alcohol, about 22% of a nitrogenous substance closely resembling the azolitmin of litmus is obtained. This is greenish-black in colour, and almost insoluble in water, alcohol, or acetone ; it absorbs ammonia gas, forming a bluish-black product, which dissolves in water, forming a red solution from which the purified azolitmin is regenerated on addition of excess of acid or salts of heavy metals. This ammonium compound is a useful indicator. Similar products are obtained with methylamine and dimethylamine. T. A. H.

The Portion of Litmus Soluble in Alcohol. Paul Scheitz (*Zeit. anal. Chem.*, 1910, **49**, 736—739. Compare preceding abstract). —The isolation of a blue colouring matter distinct from azolitmin and soluble in alcohol is described. When crude litmus is treated with dilute hydrochloric acid until no more carbon dioxide is evolved, the red solution formed slowly deposits, when warmed at 100°, a dark brown precipitate, which, when boiled with water, separates into (*a*) a finely-divided reddish powder, containing some azolitmin, but consisting chiefly of products soluble in alcohol, and (*b*) a grey-steel product, mainly composed of azolitmin, but containing a little alcohol-soluble matter.

When boiled with a mixture of alcohol (2 parts) and water (1 part), preparations *a* and *b* furnish (1) azolitmin, insoluble in aqueous alcohol, and (2) a mixture of Kane's erythrolein and erythrolitmin with a third substance, which is bright brown in colour, all of these being soluble in hot aqueous alcohol. Of these three substances the first two can be eliminated by extraction with hot acetone, leaving the third in an impure form, from which a purer form can be prepared by dissolving it in hot aqueous alcohol, filtering, and cooling, when it is deposited as bright brown powder, equivalent in weight to 1·5% of the purified litmus. This is soluble in formic acid, pyridine, or ammonia, forming a bluish-violet solution with the last-mentioned solvent. It absorbs ammonia gas, becoming hot, and forming a dark blue ammonia compound, which dissolves in water to a reddish solution. This ammonia compound is a more delicate indicator than the corresponding derivative of azolitmin (compare preceding abstract). Similar substances are formed by absorption of methylamine and dimethylamine. T. A. H.

Phycoerythrin and Phycocyanin from Ceramium rubrum (Huds.). Harald Kylin (*Zeitsch. physiol. Chem.*, 1910, **69**, 169—239. Compare Hanson, Proc., 1909, **25**, 117 ; Molisch, Abstr., 1895, i, 556 ; 1906, ii, 118 ; Gaidukov, *ibid.*, 1904, i, 439).—Details are given for the preparation of solutions of pure phycoerythrin and phycocyanin from *Ceramium rubrum*. The isolation is based on the

fact that both colouring matters can be obtained in a crystalline form by the addition of the requisite amount of ammonium sulphate to their solutions; the phycocyanin is deposited when 18 grams of sulphate, and the phycoerythrin when 25 grams of sulphate, have been added to 100 c.c. of the solution. Magnesium sulphate may also be used, but larger quantities are necessary. Phycocyanin can be precipitated in an amorphous state by completely saturating its solution with sodium chloride, but phycoerythrin is not precipitated under these conditions.

The phycoerythrin solution has a carmin-red colour, and when dilute a tinge of violet; concentrated solutions have an orange colour, and all solutions give a characteristic orange-yellow fluorescence. It gives all the characteristic reactions of a protein, including the biuret reaction (compare Hanson). The colouring matter dissolves in water containing a small amount of alkali or of neutral salts, but is deposited in a crystalline form when all salts are removed by dialysis. It is insoluble in ordinary organic solvents, but dissolves in dilute acetic acid and also in extremely dilute hydrochloric acid, yielding solutions which do not fluoresce.

The conclusion is drawn that the acid decomposes the phycoerythrin into protein and colouring matter, and that the precipitate obtained on adding a small amount of sodium carbonate to the acid solution is the colour-constituent. The addition of a trace of acid to the ordinary solution precipitates the phycoerythrin.

The small amounts of salts which are necessary to keep the colouring matter in solution are sufficient to cause complete precipitation when the solution is heated at 90°. The addition of traces of acid reduce the temperature of coagulation, and the amount of acetic acid necessary to give the ordinary protein reaction produces coagulation at 53—55°. The addition of a trace of alkali prevents coagulation.

The action of pepsin and trypsin is represented as first causing a decomposition of the phycoerythrin into protein and colour-constituents, and then the decomposition of the protein. After the digestion with pepsin, the colour-constituent can be removed by shaking with amyl alcohol. The results of analyses of phycoerythrin gave: C = 50·82, H = 7·01, N = 15·37, S = 1·60, and O = 25·20%.

The absorption spectrum of pure phycoerythrin contains three characteristic bands, two between *D* and *E*, and one between *E* and *F*. These bands have their maxima at $\lambda = 569—565$, $541—537$, and $498—492$ $\mu\mu$. On dilution the second band disappears before the third.

Phycocyanin crystallises in rhombic plates, quite different from the crystals described by Molisch. It gives the protein reactions; its solubility in water, saline solutions, and dilute alkalis is similar to that to phycoerythrin, as is also its behaviour towards acids, pepsin, and trypsin.

A solution of phycocyanin containing the smallest possible amount of salt is completely coagulated when heated at 82°, and the addition of a little acetic acid reduces this to 46—48°.

The solutions of phycocyanin exhibit two absorption bands, one between *C* and *D* and the other between *D* and *E*, the maxima being at λ 618—613 and 553—549 $\mu\mu$. J. J. S.

Sulphur Dyes. II. Hermann Wichelhaus (*Ber.*, 1910, 43, 2922—2926. Compare Abstr., 1907, i, 232; Erdmann and Schäfer, this vol., i, 718).—The distillate from 20 kilograms of cellulose (cotton) consisted of 5·7 litres of an aqueous liquid and 1 litre of an oily mass. From both of these only one phenol could be isolated, namely, phenol itself. The author has put forward the view that a sulphur dye could be formed from phenol, thus explaining the origin of sulphur dyes from cellulose. As an intermediate product, phenoquinone claims attention. Molecular-weight determinations in the case of the analogous toluquinone and thiotoluquinone confirm the original statement (*Ber.*, 1872, 5, 248) that phenoquinone has the formula $C_{18}H_{14}O_4$. When it is boiled with alkali sulphides and sulphur, or, better, heated with those substances under pressure at 200—220°, a sulphur dye is formed, which, after purification, contains C 75%, H 5%, S 12%. It is a dark brown powder, insoluble in alkaline carbonates, ammonia, and acids, but soluble in alkali sulphides. The last-named solution dyes cotton dark brown.

Phenoquinone also yields a dye free from sulphur when it is kept for ten days at the ordinary temperature in contact with sodium acetate and water. The crude product is purified by solution in sodium hydroxide, re-precipitation with acid, removal of phenol by means of steam, and final precipitation as iron salt, which is decomposed by hot hydrochloric acid. So obtained, the acid has m. p. 110°. When dissolved in sodium carbonate, it dyes cotton brown.

Fluorescein yields sulphur dyes when heated with sulphur or sulphur and sodium sulphide, but it is not possible to obtain them in a pure state. Dithiofluorescein chloride,

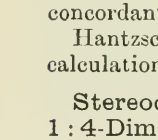
$$CS\langle\begin{matrix}C_6H_4\\--S--\end{matrix}\rangle C\langle\begin{matrix}C_6H_3Cl\\C_6H_3Cl\end{matrix}\rangle O,$$

which is not a dye, condenses in presence of sulphuric acid or anhydride to form sulphur derivatives which are dyes. R. V. S.

Velocity of the Transformation of Oxonium Bases, Colour Bases, and Cyanides into Carbinol Bases and Leucocyanides. Wolf. J. Müller (*Ber.*, 1910, 43, 2609—2613. Compare this vol., i, 407; Gerlinger, Abstr., 1904, i, 1040).—The velocity constants of various reactions studied by Hantzsch and his pupils (Abstr., 1900, i, 113, 256) have been recalculated from Hantzsch's data, and it is shown that, using the equation for a bimolecular reaction, quite concordant values for K are obtained.

Hantzsch's statement to the contrary is due to mistakes in calculation. J. J. S.

Stereochemistry of 1 : 4-Dimethyltetrahydrofuran and 1 : 4-Dimethylfuran. Angel del Campo y Cerdán (*Anal. Fis. Quim.*, 1910, 8, 227—244).—A geometrical study of the causes of the difference of stability of the two compounds (annexed formulæ) from the point of view of the "tension" theory. It is shown that the mass of the groups in the first compound causes a greater strain or deforma-



tion from the simple regular tetrahedral form, representing a carbon atom combined with four hydrogen atoms, than those of the second; the latter is therefore the more stable substance, as is actually the case.

W. A. D.

ω-Hydroxy-*s*-methylfurfuraldehyde. Henry J. H. Fenton (*Ber.*, 1910, **43**, 2795—2796. Compare Fenton and Gostling, Trans., 1899, **75**, 430; Fenton and Robinson, *ibid.*, 1909, **95**, 1338; Alberda van Ekenstein and Blanksma; Erdmann, this vol., i, 762).—Attention is drawn to the fact that the hydroxyfurfuraldehydes prepared from the ω-bromomethylfurfuraldehyde and from inulin by the action of oxalic acid are identical. They yield the same phenylhydrazone and the same oxidation product, and both are to be regarded as ω-hydroxy-*s*-methylfurfuraldehyde.

J. J. S.

Triphenylmethyl. XIX. Quinocarbonium Salts. Moses Gomberg and Lee H. Cone (*Annalen*, 1910, **376**, 183—238. Compare Abstr., 1907, i, 504; 1909, i, 144; this vol., i, 55).—Not merely salts of triphenylmethane and xanthenol, but also those derived from diphenoxanthhydrol, dinaphthaxanthhydrol, thioxanthenol, and 4 bromothioxanthenol exist in colourless benzenoid and yellow quinonoid forms. The acridol salts are also regarded as quinocarbonium salts. Diphenoxanthhydrol exists in the solid form as the colourless benzenoid carbinyl chloride, and appears to be incapable of yielding a stable coloured chloride hydrochloride; it can, however, be readily transformed by means of sulphur dioxide, sulphuric acid, or metallic halides. Dinaphthaxanthhydrol, on the other hand, yields a perfectly stable and intensely coloured chloride dichloride in addition to the colourless carbinol chloride.

Xanthhydryl chloride, $O<^{C_6H_4}_{C_6H_4}>CHCl$ (compare Werner, Abstr., 1902, i, 50), can be prepared by the action of hydrogen chloride on xanthhydrol in absolute ethereal solution. It is extremely sensitive to traces of moisture, but can be obtained in colourless needles, m. p. 73—75° after sintering at 71°. When further heated, hydrogen chloride is evolved, and at 170—175° the evolution is rapid. Hydrogen chloride is also evolved when the salt is heated with xylene or nitrobenzene, but whether dixanthylene is formed or not has not been determined. It does not yield a stable quinonoid hydrochloride, but the following double salts have been prepared: *zincichloride*, $C_{13}H_9OCl,ZnCl_2$, yellow, granular precipitate; ferrichloride,

$$C_{13}H_9OCl,FeCl_3,$$

m. p. 193° (compare Werner); *periodide*, $C_{13}H_9OCl,I_4$, prepared from benzene solutions, dark blue crystals, m. p. 90°.

Xanthhydryl bromide, $O:(C_6H_4)_2:CHBr$, is much more stable than the chloride, and crystallises from light petroleum solutions in long, colourless needles, m. p. 88—90°, which turn yellow when kept. The pure quinocarbonium salt has not been obtained, but the following double salts are described: *zincibromide*,

$$C_{13}H_9OBr,ZnBr_2,$$

slender, orange-yellow crystals; *periodide*, dark blue crystals with four or six atoms of iodine.

Xanthhydryl perchlorate, $C_{13}H_9O\cdot ClO_4$, forms dark red crystals, m. p. 208—209°.

Dinaphthaxanthen is best prepared by heating pure *p*-dihydroxynaphthylmethane (Manasse, Abstr., 1894, i, 577) with glacial acetic acid in a current of hydrogen chloride. Dinaphthaxanthhydrol can be prepared by Fosse's methods (Abstr., 1902, i, 171).

Dinaphthaquinoxanthhydryl chloride hydrochloride,

$$C_{10}H_6\begin{<}CH{:}C\cdot C_6H_4\\ O{-}C{:}CH{-}\end{>}CHCl,HCl,$$

prepared by the action of acetyl chloride and hydrogen chloride on a benzene solution of the hydrol or on the anhydride in chloroform solution, crystallises in dark red needles, m. p. 228—229° (decomp.), and is extremely stable. When a current of air is passed through its toluene solution at 100°, hydrogen chloride is evolved, and *dinaphthaxanthhydryl chloride*, $O\begin{<}C_{10}H_6\\ C_{10}H_6\end{>}CHCl$, is precipitated on the addition of light petroleum to the concentrated solution as slender, colourless needles, m. p. 205—206°, which are comparatively stable. The *zincichloride*, $C_{21}H_{13}OCl,ZnCl_2$, forms a stable, orange-red, crystalline mass, and the *periodide*, $C_{21}H_{13}OCl,I_2$, is precipitated when iodine is added to a benzene solution of the chloride. *Dinaphthaquinoxanthhydryl bromide hydrobromide*, $C_{21}H_{13}OBr,HBr$, forms a red, crystalline mass, and is even more stable than the hydrochloride. The *perchlorate*, $C_{21}H_{13}O\cdot ClO_4$, forms red crystals with a golden reflex, is not molten at 260°, and is only slowly decomposed by water. Dinaphthaxanthen reacts with a carbon disulphide solution of bromine, yielding a red *dinaphthaxanthhydryl bromide perbromide* according to the equation: $O{:}(C_{10}H_6)_2{:}CH_2 + 2Br_2 = O{:}(C_{10}H_6)_2{:}CHBr\cdot Br_2 + HBr$, even when less than the theoretical amount of bromine is used. Chlorine reacts with a carbon tetrachloride solution of the xanthen, yielding an insoluble chloride perchloride.

Phenylthioxanthenol, prepared by a modification of Bünzly and Decker's method (Abstr., 1904, i, 912), reacts with a mixture of acetyl and hydrogen chlorides in chloroform solution, yielding *phenylquinothioxanthenyl chloride hydrochloride*, $\begin{matrix}HCl,C\\ \\ CH\end{matrix}\begin{matrix}HCl\cdot CH{:}C{-}{-}{-}S\\ \\ =CH\cdot C{:}CPh\end{matrix}\!\!>C_6H_4$, in the form of dark red crystals, the colour of which is much deeper than that of the corresponding oxygen compound. When dry air is led through a benzene solution of the red compound, hydrogen chloride is evolved and *phenylthioxanthenyl chloride*, $S\begin{<}C_6H_4\\ C_6H_4\end{>}SPhCl$, is formed. This crystallises from light petroleum in colourless prisms, m. p. 114—115°, after sintering at 110°, and turns red on exposure to the air. The chloride reacts with "molecular" silver in the presence of dry benzene, yielding a brownish-red, unsaturated compound, which is stable in the absence of air, but combines readily with oxygen, yielding the *peroxide*, $S{:}(C_6H_4)_2{:}CPh\cdot O\cdot O\cdot CPh{:}(C_6H_4)_2{:}S$,

which crystallises in colourless, hexagonal prisms, m. p. 187—188°, after sintering at 175—180°.

The *2-phenylthiol-4-bromobenzoic acid*, $C_{13}H_9O_2SBr$, prepared by Goldberg's method (Abstr., 1905, i, 59), crystallises from glacial acetic acid, has m. p. 230—231°, and when warmed with concentrated sulphuric acid and then diluted yields *4-bromothioxanthone*,

$$S<\begin{matrix}C_6H_4\\C_6H_3Br\end{matrix}>CO,$$

as slender, yellow needles, m. p. 165°, which reacts with phenyl magnesium bromide, yielding *4-bromo-9-phenylthioxanthenol*,

$$S<\begin{matrix}C_6H_4\\C_6H_3Br\end{matrix}>CPh\cdot OH,$$

as an oil, from which a few crystals, m. p. 75—80°, can be obtained. *4-Bromo-9-phenylquinothioxanthenyl bromide hydrobromide*,

$$C_{19}H_{12}SBr_2,HBr,$$

forms dark red needles, which are immediately decomposed by moisture. *4-Bromo-9-phenylthioxanthenyl bromide*,

$$S<\begin{matrix}C_6H_4\\C_6H_3Br\end{matrix}>CPhBr,$$

is usually slightly coloured, has m. p. 159°, after sintering at 150°, and after treatment with silver it does not yield a peroxide. In this respect it resembles the monohalogenated triphenylmethyl halides, as also in the readiness with which the two atoms of bromine are replaced by chlorine when the bromide is shaken with benzene and silver chloride.

4-Chloro-9-phenylquinothioxanthenyl chloride hydrochloride,

$$C_{19}H_{12}SCl_2,HCl,$$

obtained by shaking the corresponding tribromo-derivative with benzene and silver chloride, or by saturating the benzene solution with hydrogen chloride, is somewhat paler in colour than the bromide, and gives up hydrogen chloride when dry air is passed through its benzene solution at the ordinary temperature. The product, *4-chloro-9-phenylthioxanthenyl chloride*, $C_{19}H_{12}SCl_2$, is readily soluble in all solvents, and has not been obtained pure. *9-Phenylthioxanthenyl perchlorate*, $C_{19}H_{13}S\cdot ClO_4$, crystallises in slender, dark red plates, m. p. 195—210°, after sintering at 150°, and *thioxanthone perchlorate*, $C_{13}H_9OS\cdot ClO_4$, in transparent, brown prisms.

A number of compounds of dimethylpyrone, benzo-γ-pyrone, xanthone, aldehydes, ketones, and phenols with acids have been prepared. Many of them have been described previously (compare Collie and Tickle, Trans., 1899, **75**, 710; Feist, Abstr., 1892, 811; Baeyer and Villiger, Abstr., 1901, i, 658; Vorländer, Abstr., 1903, i, 495; Werner, Abstr., 1902, i, 686; Ruhemann, Trans., 1900, **77**, 985, 1123), but the following are new. Dimethylpyrone derivatives: $(C_7H_8O_2)_2ZnCl_2$, colourless crystals, m. p. 200°; *zincichloride*, $(C_7H_8O_2,HCl)_2ZnCl_2$, colourless, hygroscopic crystals; $C_7H_8O_2,HgCl_2$, colourless crystals, m. p. 149°; *mercurichloride*, $C_7H_8O_2,HCl,HgCl_2$; *ferrichloride*, $3C_7H_8O_2,2FeCl_3$, lemon-yellow crystals, m. p. 173—174°; *hydrobromide*, $C_7H_8O_2,HBr$, m. p. 194—196°, after sintering at 188°; $2C_7H_8O_2,ZnBr_2$, colourless crystals, m. p. 204—205°. Derivatives of

benzo-γ-pyrone: *hydrochloride*, $C_9H_6O_2$,HCl, m. p. 101—102° (decomp.); $C_9H_6O_2$,$ZnCl_2$, colourless crystals, m. p. 250—251°, after sintering at 205°; *zincichloride*, $(C_9H_6O_2,HCl)_3ZnCl_2$; $C_9H_6O_2$,$HgCl_2$, colourless crystals; *hydrobromide*, $C_9H_6O_2$,HBr, m. p. 175°, after sintering at 169°; *hydrobromide periodide*, dark blue crystals.

The hydrochloride and hydrobromide of dimethylpyrone are decomposed when heated with benzene and a current of dry air drawn through the solution, and the salts of benzo-γ-pyrone are even less stable. Dimethylpyrone does not appear to react with phenyl magnesium bromide.

Although Perkin (Trans., 1896, 69, 1439) states that xanthone does not combine with acids, the following compounds have been prepared: *xanthone hydrochloride periodide*, prepared by passing hydrogen chloride into a carbon disulphide solution of xanthone and iodine; *xanthone hydrobromide*, $C_{13}H_9O_2Br$, is unstable and forms pale yellow crystals; the *perbromide*, $C_{13}H_8O_2$,HBr,Br_2, forms orange-coloured crystals and gives up bromine readily; *β-phenonaphthaxanthone hydrobromide*, $C_{17}H_{10}O_2$,HBr, forms yellow needles; *5-methoxyxanthone hydrobromide*, $C_{14}H_{10}O_3$,HBr, pale yellow crystals, and *xanthone stannichloride*, $(C_{13}H_8O_2)_2SnCl_4$, pale yellow crystals, m. p. 245°.

These compounds are compared with the additive compounds formed by the union of carbonyl derivatives with acids and salts. In the latter group of additive compounds the acid, for example, hydrogen chloride, is, almost undoubtedly, added on to the carbonyl group, and it is suggested that probably the same type of reaction takes place with dimethylpyrone, xanthone, etc. The products are probably not salts, and their decomposition into oxygen compound plus acid is probably not a process of hydrolysis, but of dissociation (addenda-dissociation of Vorländer).

Fluorenone hydrobromide periodide, $C_{13}H_8O$,HBr,I_3, forms coloured crystals; *phenanthraquinone hydrobromide*, $C_{14}H_8O_2$,HBr, is unstable, and anthraquinone does not appear to yield a hydrobromide. Anisaldehyde hydrobromide (compare Vorländer) is stable, and can be prepared at the ordinary temperature. *p*-Hydroxybenzaldehyde, resorcylaldehyde, piperonal, vanillin, and β-naphtholaldehyde all yield comparative stable, yellow *hydrobromides*.

Phenols which can react in the tautomeric ketonic forms can also form hydrobromides, for example, orcinol, phloroglucinol, and quinol, whereas resorcinol, pyrogallol, guaiacol, and the methyl ethers of resorcinol, quinol, and pyrogallol do not combine with hydrogen bromide.

The application of the quinocarbonium theory to the cases of pararosaniline, phenylated rosanilines, amino-azines, aurin, phenolphthalein, fluorescein, and fluorone is discussed. The theory accounts for the fact that phenolphthalein is incapable of yielding a coloured hydrobromide, that fluorescein yields a mono-hydrobromide (Hewitt and Tervet, Trans., 1902, 81, 663), and dimethylfluoran a *dihydrobromide*, $C_{22}H_{16}O_3$,2HBr, slender, orange-yellow crystals. J. J. S.

Brominated and Iodinated Products of Curare Alkaloids Józef Buraczewski and Z. Zbijewski (*Bull. Acad. Sci. Cracow*, 1910, 352—354).—The two alkaloids, curine and tubocurarine, in commer-

cial tubocurare from the bamboo have been examined with regard to their behaviour towards bromine and iodine. Curine, in ethereal solution, gives with bromine a straw-yellow precipitate, probably of a dibromo-derivative, but does not yield a precipitate with iodine. An alcoholic solution, however, by treatment with iodine in carbon disulphide gives a brownish-red precipitate, which dissolves very easily in alkalis or in aqueous ammonia, being re-precipitated by acids in the form of an almost black substance containing 49·65% of iodine. Curine, therefore, resembles strychnine in its behaviour towards bromine, but not towards iodine. An alcoholic solution of tubocurarine and iodine in carbon disulphide give a similar precipitate of like properties. The formation of these iodinated products is of use in the examination of crude tubocurare, because the colour reactions of curine and tubocurarine are applicable only to the isolated alkaloids, not to crude tubocurare. C. S.

Action of Chlorine on Strychnine, Brucine, Cinchonine, Quinine, and Other Alkaloids. Józef Buraczewski and Z. Zbijewski (*Bull. Acad. Sci. Cracow*, 1910, 355—362).—On account of the oxidising action of chlorine, chlorinated derivatives of the alkaloids are more difficult to prepare than brominated or iodinated derivatives. By passing a slow current of dry chlorine over the well-cooled and shaken dry alkaloids, the authors find that chlorinated products are obtained containing usually more halogen than is the case in the usual methods of chlorination; heat is developed and frequently hydrogen chloride given off, although sometimes only after some time. By this process, strychnine absorbs five atoms of chlorine, brucine three, cinchonine four, cinchonidine three, quinine six, quinidine six, thebaine four, and morphine one. In these chlorinated alkaloids at least a part of the halogen is bound in the same way as the halogen in the brominated or iodinated derivatives, because all of the products except the chlorinated morphine yield with warm water an insoluble precipitate and a soluble salt of a chlorinated base. C. S

Action of Acetone on Di-iodostrychnine and on the Brominated Products of Strychnine and of Some Other Alkaloids. Józef Buraczewski and Mieceslas Dziurzyński (*Bull. Acad. Sci. Cracow*, 1910, 363—366).—Complicated reactions take place during the prolonged boiling necessary for the solution of di-iodostrychnine (Abstr., 1908, i, 1007) in acetone. Two colourless, non-poisonous, crystalline products are obtained, which do not exhibit the properties of strychnine or of its salts. Strychnine hydriodide and periodide, $C_{21}H_{22}O_2N_2I_2,HI$, are also produced, together with iodoacetone. Dibromostrychnine and tetrabromostrychnine (and also pentabromoquinine) likewise cause the formation of bromoacetone when they are boiled with acetone. The formation of these halogenated acetones is regarded as evidence that the method of union of the two iodine atoms in di-iodostrychnine is the same as that of two bromine atoms in dibromo- or in tetrabromo-strychnine. C. S.

Oxidation Products of Brominated Strychnines. I. Józef Buraczewski and T. Nowosielski (*Bull. Acad. Sci. Cracow*, 1910, 154—162).—On account of the scarcity of characteristic oxidation products of strychnine and of their importance for the determination of its constitution, the authors have commenced a more thorough examination of the precipitates obtained by Buraczewski and Dziurzyński (Abstr., 1909, i, 672). These authors found that by warming dibromostrychnine with water a precipitate is formed; the bromostrychnine obtained from the filtrate yielded by bromination a mixture of tri- and tetra-bromostrychnines, which likewise yielded a precipitate when warmed with water. The basic substance obtained from the aqueous filtrate in the latter case has been brominated, yielding a product which again gives a precipitate when warmed with water. The first-mentioned precipitate dissolves almost completely in alcohol, but the others are separated by this solvent into a soluble and an insoluble portion. The insoluble portions behave alike towards alkalis, acids, and solvents, and are recrystallised, after being mixed, from hot acetic acid by the addition of water, yielding a *substance*, $C_{21}H_{20}O_3N_2Br_3$, which is dextrorotatory, non-poisonous, has no bitter taste, and is provisionally called *tribromostrychnine oxide*. The portions soluble in alcohol are combined and purified by precipitating the alcoholic solution with water containing hydrochloric acid; the product is amorphous (it has since been obtained crystalline in very small quantity), optically inactive, non-poisonous, and has a composition approximating to the formula $C_{21}H_{22}O_4N_2Br_3$. The aqueous filtrate, from which the last-mentioned precipitate has been separated, contains a substance which has pronounced basic properties, is lævorotatory, and is non-poisonous, but has an intensely bitter taste. C. S.

Alkaloids in the Roots of Sanguinaria canadensis Tad. Kóźniewski (*Bull. Acad. Sci. Cracow*, 1910, 235—246).—Sanguinarine, isolated by Dana in 1828 from the roots of *Sanguinaria canadensis*, and proved by Schiel in 1842 to be identical with chelerithrine obtained by Probst from *Chelidonium majus*, has been shown to be a mixture of three alkaloids by Schmidt and his collaborators, who found that the roots of *Sanguinaria* contain five alkaloids, namely, sanguinarine (red salts), chelerithrine (yellow salts), protopine, and β- and γ-homochelidonine (colourless salts). The last two are easily separated from the first three by their solubility in aqueous ammonia, but the separation of sanguinarine, chelerithrine, and protopine presents very great difficulties. The author describes a comparatively simple method which depends on the formation of sparingly soluble salts. The alcoholic extract of the powdered roots is evaporated, and the residue is treated with 5% and with 10% acetic acid. Three-quarters of the mass remains undissolved (*P*), and is worked for sanguinarine as described below. The acetic acid solutions are cooled and treated with 40% sulphuric acid, whereby a crystalline precipitate is formed, which is collected after forty-eight hours and yields pure chelerithrine after further purification. The filtrate is cooled in a freezing mixture, and just basified with ammonia. The resulting precipitate is extracted with hot dilute acetic acid, and the solution is

treated with an excess of 40% sulphuric acid. The yellow, crystalline precipitate obtained yields a further quantity of chelerithrine, whilst the filtrate by treatment with ammonia gives a violet precipitate. This is dissolved in 10% acetic acid, and the solution treated with an excess of sulphuric acid. A third precipitate is thus obtained containing a considerable quantity of chelerithrine and sanguinarine; the precipitate obtained by adding ammonia to the filtrate is dissolved in 10% sulphuric acid, and the solution is treated with more sulphuric acid, whereby a fourth crystalline precipitate containing chelerithrine and sanguinarine is obtained, the filtrate being worked for protopine, which is finally isolated in the form of its hydrochloride.

The residue (*P*) is ground with kieselguhr and heated for three hours with 20% sulphuric acid. The red solution deposits a scarlet precipitate on cooling, from which pure sanguinarine is obtained by further purification. The fact that the residue requires prolonged heating with sulphuric acid for solution is taken as evidence that sanguinarine is present in the roots in the form of a stable compound which yields the alkaloid by hydrolysis.

From his analyses the author concludes that sanguinarine separates from solutions containing alcohol in crystals containing Et·OH; the m. p. of such crystals is 212°. Sanguinarine forms a *periodide*, $C_{20}H_{15}O_4NI_2,HI$, m. p. 205°, and chelerithrine, a *periodide*,

$$C_{21}H_{17}O_4NI_2,HI,$$

m. p. 225°, crystallising in ruby-red needles. C. S.

Reactions of 2 : 4 : 6-Trihydroxypiperidine Trisulphite. Julius Schenkel (*Ber.*, 1910, 43, 2597—2601).—The additive compound of pyridine and sodium hydrogen sulphite, which is regarded as the trisulphite ester derived from 2 : 4 : 6-trihydroxypiperidine (compare Bucherer and Schenkel, Abstr., 1908, i, 452), can be estimated by boiling with alkali hydroxide solution and titrating the ammonia evolved. It also reacts with a solution of *p*-nitrobenzenediazonium chloride in the presence of an excess of sodium hydrogen carbonate, yielding a blood-red solution, which changes to yellow on the addition of a slight excess of acid; in acid solution a voluminous, yellow precipitate is obtained, which decomposes rapidly, yielding a resinous product free from sulphur.

Benzoyl chloride and alkali react with the ester, yielding benzoic anhydride, and a hot solution of the ester rapidly transforms phenylhydrazine into its *N*-sulphonic acid.

When boiled with alkalis, the ester yields ammonia, alkali sulphite, and glutaconaldehyde, the last of which was isolated as its dianilide, NPh:CH·CH:CH·CH:CH·NHPh (compare Zincke, Abstr., 1904, i, 448; Koenig, *ibid.*, i, 817), the hydrochloride of which crystallises in red needles, m. p. 141—143°.

When the ester is neutralised with sodium hydroxide solution, and then boiled with phenylhydrazine for three hours, ammonia is evolved, and the *sodium* salt of *1-anilino-2 : 4 : 6-trihydroxypiperidine trisulphite*, $C_{11}H_{13}O_9N_2S_3Na_3,2H_2O$, is obtained as colourless crystals, which begin to decompose at 180°. J. J. S.

The Action of Sulphites on Pyridine. Fritz Reitzenstein and Wilhelm Breuning (*Ber.*, 1910, 43, 2939—2940. Compare Schenkel, preceding abstract).—A claim for priority. The existence of Zincke's glutaconaldehyde, which Schenkel has isolatad in the form of its dianilide, had already been demonstrated by the authors, who obtained from it the ditoluidide (Breuning, *Diss.*, Würzburg, 1909).

R. V. S.

Additive Compounds of Mercury Salts and Aromatic Bases. Wilhelm Staronka (*Bull. Acad. Sci. Cracow*, 1910, 372—398).—The great solubility of mercury salts in organic bases is due to the formation of additive compounds of the salts and the solvent. The salts of mercury which have been examined are the cyanide, chloride, bromide, and iodide; the bases used are aniline, pyridine, and quinoline. Exactly weighed amounts of a salt and a base are heated in a sealed tube until fusion is complete. The tube is allowed to cool until crystals, generally of an additive compound, separate, and is then carefully re-heated until only a pair of crystals remain; the temperature at which the two crystals persist unchanged for a long time is taken as the temperature of solidification of the mixture under examination. The results are expressed graphically, the molecular concentrations of one constituent being plotted as abscissæ, the corresponding temperatures of solidification as ordinates. The curves obtained are of two types, one kind exhibiting a maximum corresponding with the m. p. of the additive compound, and the other kind showing breaks, indicating the transition of one solid phase into another. The compositions of the additive compounds can be determined directly from curves of the first type. In the case of mixtures giving curves of the second type, it is necessary to isolate the solid phase before its composition can be determined by analysis. The isolation is a matter of some difficulty, because the solid phase is only stable within a definite range of temperature; a method is described by which the separation can be effected by the use of a centrifugaliser in an air-bath. Of the bases examined, pyridine shows the greatest tendency to form additive compounds; of the salts, the cyanide. The most frequently occurring types of additive compounds are $HgX_2,2B$ and HgX_2,B, where B = 1 mol. of the base. The following new additive compounds have been obtained: $Hg(CN)_2,6C_5NH_5$; $Hg(CN)_2,3C_5NH_5$; $2Hg(CN)_2,3C_5NH_5$; $Hg(CN)_2,C_5NH_5$; $HgBr_2,C_5NH_5$, m. p. 123°; $3HgBr_2,2C_5NH_5$, m. p. 134°; HgI_2,C_5NH_5, m. p. 90°; $Hg(CN)_2,3C_9NH_7$; $HgBr_2,2C_9NH_7$; $HgI_2,2C_9NH_7$; $Hg(CN)_2,4PhNH_2$ (metastable); $HgBr_2,PhNH_2$, m. p. 124°.

C. S.

Theories of the Constitution of Double Salts. Paul Pfeiffer [with B. Friedmann and H. Rekate] (*Annalen*, 1910, 376, 310—344).—The constitution of the double salts formed by metallic halogenides has been explained by various theories, of which the Blomstrand-Remsen and the Werner are the most prominent. According to the former, the constitution is represented by, for example,

$Cl>P<^{Cl:ClK}_{Cl:ClK}$, the addition occurring by means of tervalent halogen atoms, whilst the constitution is expressed by $[PtCl_6]K_2$ by the well-known Werner theory.

The following compounds have been prepared in order to differentiate between these two theories. They are double salts of tin halogenides, all of the type SnA_n, but containing different numbers of halogen atoms, and alkali halogenides or similar compounds. According to the Blomstrand-Remsen theory, the number of molecules of alkali halogenide added is a function of the number of halogen atoms in the tin halogenide; by the Werner theory the number added is independent of the number of halogen atoms in the tin halogenide. The existence of compounds, such as $SnPh_3Cl,2C_5NH_5,2HCl$ and

$$SnPh_3Br,2C_5NH_5,2HBr,$$

is contrary to the Blomstrand-Remsen theory.

Pyridinium stannichloride, $2Py,H_2SnCl_6$, obtained from pyridine and stannic chloride in concentrated hydrochloric acid, and *quinolinium stannichloride*, $2Qn,H_2SnCl_6$ ($Qn = C_9NH_7$), m. p. 266°, similarly prepared, form colourless crystals; the *stannibromides*, $2Py,H_2SnBr_6$ and $2Qn,H_2SnBr_6$, m. p. 258—261°, are yellow. Pyridinium stanni-iodide, $2Py,H_2SnI_6$, prepared from pyridine hydriodide and stannic iodide in alcoholic hydrogen iodide, forms dark brown leaflets (compare Rosenheim and Aron, Abstr., 1904, ii, 411. The substance described by these authors as forming bluish-black needles is pyridinium periodide, $HPyI_3$). *Pyridinium stannimethylpentachloride*, $[SnCl_5Me]2HPy$, and the *quinolinium* salt, $[SnCl_5Me]2HQn$, m. p. 200° (decomp.), obtained from methylstannic acid and pyridine or quinoline in cold concentrated hydrochloric acid, form colourless crystals. *Pyridinium stannimethylpentabromide*, $[SnBr_5Me]2HPy$, m. p. 165—172° (decomp.), and the *quinolinium* salt, $[SnBr_5Me]2HQn$, m. p. 80—145° (decomp.), obtained from alcoholic tin methyl bromide and pyridine or quinoline in concentrated hydrobromic acid, crystallise in yellow needles. Stannimethylpentaiodides cannot be prepared. *Pyridinium stannidimethyltetrachloride*, $[SnCl_4Me_2]2HPy$, m. p. 143—144°, and the *quinolinium* salt, $[SnCl_4Me_2]2HQn$, m. p. 167°, obtained from tin dimethyl chloride (m. p. 108°, not 90°) and pyridine or quinoline hydrochloride in methyl-alcoholic hydrogen chloride, form colourless needles. The corresponding *stannidimethyltetrabromide*, $[SnBr_4Me_2]2HPy$, m. p. 108—112°, and $[SnBr_4Me_2]2HQn$, m. p. 134°, prepared in a similar manner, are colourless, but gradually become yellow by keeping. The following six compounds are also prepared in a similar manner: $[SnCl_4Et_2]2HPy$, m. p. 118—122°, colourless prisms;

$$[SnCl_4Et_2]2HQn,$$

m. p. 134—135°, stable, colourless needles; $[SnBr_4Et_2]2HPy$, m. p. 90—99°, colourless needles; $[SnBr_4Et_2]2HQn$, m. p. 120—124°, colourless needles; $[SnCl_4Pr^{\alpha}_2]2HPy$, m. p. 114°, colourless plates; $[SnBr_4Pr^{\alpha}_2]2HPy$, m. p. 100—114°, colourless leaflets. *Pyridinium stannidiphenyltetrachloride*, $[SnCl_4Ph_2]2HPy$, m. p. 186°, obtained from stannic diphenyl oxide and pyridine hydrochloride in saturated methyl- or ethyl-alcoholic hydrogen chloride, and the *quinolinium* salt, $[SnCl_4Ph_2]2HQn$, m. p. 133—140°, similarly prepared, form colourless

crystals. The corresponding *bromo*-compounds, $[SnBr_4Ph_2]2HPy$, m. p. 195°, and $[SnBr_4Ph_2]2HQn$, m. p. 119—129° or 130—131° (different samples), are likewise colourless. *Pyridinium stannitriphenyltrichloride*, $[SnClPh_3]2HPy$, m. p. 169—170°, obtained from stannic triphenyl chloride (m. p. 112—113°, not 106°) and pyridine hydrochloride in methyl-alcoholic hydrogen chloride, and *pyridinium stannitriphenyltribromide*, $[SnBr_3Ph_3]2HPy$, m. p. 146—153° or, after resolidification, 194°, similarly prepared, form colourless crystals, and are the only substances which can be obtained from tin halogenides of the type SnR_3Cl. C. S.

Betaines of Pyridinium-maleic and Pyridiniumacrylic Acids and their Salts. Paul Pfeiffer and A. Langenburg [in part with Miss Birencweig] (*Ber.*, 1910, **43**, 2926—2939. Compare O. Lutz, following abstract).—When dibromosuccinic acid is treated with pyridine, a mixture of pyridine salts is obtained, which, on warming, evolves carbon dioxide, and leaves a residue from which two substances can be isolated. Of these, one contains ionic bromine, has acid properties, and is identical with the compound obtained from pyridine and α-bromoacrylic acid. To it is therefore ascribed the structure of α-pyridiniumacrylic acid bromide, $C_5H_5NBr\cdot C(:CH_2)\cdot CO_2H$. The other substance yields an additive product with hydrogen bromide, which, on heating, loses carbon dioxide and is converted into α-pyridiniumacrylic acid bromide, so that it probably has the structure of a betaine of pyridinium-maleic acid, $\begin{matrix} C_5H_5N\cdot C:CH\cdot CO_2H \\ | \quad\quad | \\ O\cdot CO \end{matrix}$ or $\begin{matrix} C_5H_5\cdot N\text{——}C\cdot CO_2H \\ | \quad\quad\quad || \\ O\cdot CO\cdot CH \end{matrix}$, the maleic structure being more probable than the fumaric, because quinoline and dibromosuccinic acid yield quinoline bromomaleate. The salts described give with alkalis yellow solutions, becoming blood-red (compare the colour reactions of dinitrophenyl pyridinium salts: Zincke, Abstr., 1907, i, 625).

Dibromosuccinic acid and excess of pyridine on standing for two days at the ordinary temperature yield the *tripyridine* salt,

$$CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H,3C_5H_5N,$$

as a white powder, which when kept over sulphuric acid loses pyridine, forming the *monopyridine* salt, $C_4H_4O_4Br_2\cdot C_5H_5N$, which after crystallisation forms colourless needles, m. p. about 143° (with evolution of gas).

Pyridine bromomaleate, $C_4H_3O_4Br,C_5H_5N$ (from bromomaleic acid in ethereal solution), is a white, crystalline precipitate, m. p. 94—100°. *Pyridine bromofumarate*, $C_4H_3O_4Br,C_5H_5N$, may be prepared in the same way.

Quinoline bromomaleate, $C_4H_3O_4Br,C_9H_7N$, is obtained on heating dibromosuccinic acid for some hours with quinoline; it forms colourless needles, m. p. 114—115° (with evolution of gas), and yields bromomaleic acid on treatment with ammonia.

The *betaine* of *pyridinium-maleic acid* is obtained by heating dibromosuccinic acid with pure pyridine for one hour at 60—70°. The

α-pyridiniumacrylic acid bromide, which is also produced, is removed by the addition of a little water, in which it is very soluble. The betaine becomes brown at 195°. Sodium carbonate dissolves it with evolution of carbon dioxide. When the substance is dissolved in concentrated hydrochloric acid and evaporated on the water-bath, *pyridiniummaleic acid chloride*, $C_5H_5NCl\cdot C(CO_2H):CH\cdot CO_2H$, is obtained; it crystallises in small white colourless tablets, which decompose at 150° with evolution of gas, having become brown a few degrees previously. The *bromide* may be obtained similarly, or, better, (1) by adding the betaine to concentrated hydrobromic acid until the salt separates out; (2) by evaporating over soda-lime a solution of the betaine in concentrated hydrobromic acid. It forms colourless, prismatic crystals, which decompose at 170°. On heating it to 110°, α-pyridiniumacrylic acid bromide is obtained.

α-Pyridiniumacrylic acid bromide is also obtained by warming pyridine with dibromosuccinic acid (*v.s.*), bromomaleic acid, bromofumaric acid, αβ-dibromopropionic acid, or α-bromoacrylic acid. It forms colourless needles, m. p. 216° (decomp.). With moist silver oxide it gives the betaine in solution. It gives precipitates with potassium dichromate, gold and platinum solutions. *α-Pyridiniumacrylic acid chloride*, $C_8H_8O_2NCl,H_2O$, is prepared from the bromide by the action of moist silver oxide followed by hydrochloric acid; it forms colourless needles, m. p. 195° (decomp.). The *platinochloride*,

$$(C_8H_8O_2N)_2PtCl_4,4H_2O,$$

darkens on heating, and decomposes at 196°. The *platinichloride*, $(C_8H_8O_2N)_2PtCl_6,4H_2O$, decomposes at 200°. The *picrate*,

$$C_8H_8O_2N\cdot O\cdot C_6H_2(NO_2)_3,$$

has m. p. about 158° (decomp.). R. V. S.

Characteristic Reaction of Maleic Acid. Oscar Lutz (*Ber.*, 1910, **43**, 2636—2641).—Anhydropyridiniumsuccinic acid (pyridineaminosuccinic acid, Abstr., 1901, i, 8) is also formed when *dl*-bromosuccinic acid is treated with pyridine under the conditions described by Dubreuil (Abstr., 1904, i, 189), and is the substance described by Dubreuil as pyridine hydrogen fumarate. The anhydro-compound can also be obtained from maleic acid, for example, (*a*) when pyridine hydrogen maleate is heated at its melting point (105°) for 15—20 minutes; (*b*) by keeping an aqueous-alcoholic or methyl-alcoholic solution of pyridine and maleic acid at the ordinary temperature for several weeks.

Anhydropyridiniumsuccinic acid, $C_5H_5N<\begin{matrix}CH(CO_2H)\cdot CH_2\\ |\\ O\cdot CO\end{matrix}$ or $C_5H_5N<\begin{matrix}O\cdot CO\\ |\\ CH\cdot CH_2\cdot CO_2H\end{matrix}$, has m. p. 192°, and its solubility in water at 18° is 1·65.

This reaction of maleic acid with pyridine is used as an argument in favour of the structural formula $CO_2H\cdot CH<\begin{matrix}O\\ |\\ CH_2\end{matrix}>CO$, for maleic acid. J. J. S.

Conversion of Hydrogenised Carbazoles into Derivatives of 2-Aminodiphenyl. Julius von Braun (*Ber.*, 1910, 43, 2879—2881).—In the form of their benzoyl derivatives, the hexahydrocarbazole compounds obtained by the reduction of the corresponding tetrahydrocarbazoles, prepared from *cyclo*hexanones by Fischer's indole synthesis, are readily ruptured by phosphorus pentachloride. Thus hexahydrocarbazole is converted into its *benzoyl* derivative, b. p. about 270°/10 mm., which yields 20—25% of 2-benzoylaminodiphenyl when heated with phosphorus pentachloride, first on the water-bath and finally at 120°. In a similar manner, 1-benzoyl-4-methylhexahydrocarbazole yields 2-*benzoylamino*-4′-*methyldiphenyl*, $C_6H_4Me{\cdot}C_6H_4{\cdot}NHBz$, m. p. 122°. C. S.

Tricyclic Quinolines. Walther Borsche [with R. Schmidt, H. Tiedtke, and W. Rottsieper] (*Annalen*, 1910, 377, 70—123).—Quinoline derivatives containing a third ring condensed on the pyridine nucleus in positions 2 : 3 or 3 : 4 have been prepared by the three following methods: 1. Condensation of primary arylamines with semicyclic ketones obtained from alicyclic ketones and esters. 2. Condensation of alicyclic ketones containing the grouping $\cdot CO{\cdot}CH_2\cdot$ with *o*-acylanilides. 3. Condensation of isatic acid with alicyclic ketones to acids of the desired bases, and subsequent elimination of carbon dioxide.

The products, for example, $C_6H_4<\begin{matrix}CH{:}C{\cdot}CH_2\\ |\\ N{=}C{\cdot}CH_2\end{matrix}>CH_2$ and

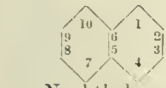
$$C_6H_4<\begin{matrix}CH{:}C{\cdot}CH_2{\cdot}CH_2\\ |\\ N{=}C{\cdot}CH_2{\cdot}CH_2\end{matrix}>CH_2,$$

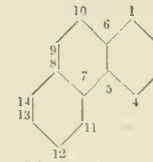
are regarded as 2:3-disubstituted quinolines, and are termed 2 : 3-trimethylenequinoline and 2 : 3-pentamethylenequinoline. The corresponding tetramethylene compounds are regarded as derived from tetrahydroacridine.

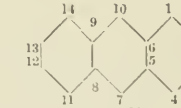
The general nomenclature of cyclic systems is discussed. The Greek capitals *gamma* Γ, *tau* T, and *pi* Π are suggested for a bridge, an acetylene linking, and a diagonal linking respectively; pinene is thus 1-methyl-$\Gamma^{2(4)}$-dimethylmethylene-$\Delta^{1(6)}$-*cyclo*hexene, camphane is 1-methyl-$\Gamma^{1(4)}$-dimethylmethylene*cyclo*hexane, tropan is $\Gamma^{1(4)}$-methylimino-*cyclo*heptane, thujone is 1-methyl-4-*iso*propyl-$\Pi^{4(6)}$*cyclo*hexan-2-one, and Moycho and Zienkowski's tricyclene (Abstr., 1905, i, 711) is 1 : 1-dimethyl-$\Gamma^{2(5)}$-methylene-$\Pi^{5(7)}$-*cyclo*heptane.

The following considerations are of importance in the numbering of the atoms of ring systems. 1. The system should indicate as far as possible the analogies in the structure of closely related compounds, for example, anthracene, xanthen, and acridine, phenanthrene and phenanthridine, etc. 2. The system should admit a numbering of the analogous reduced cyclic compounds without any alterations in the relative numbering of the substituents. The conditions would be fulfilled by the following system. The cyclic system is so written that as many directly condensed rings as possible lie on a straight line. *Each* atom of a ring system is numbered, including, for example (unlike the system adopted in Richter's Lexikon der Kohlenstoff-Verbindungen), the carbon atoms common to two rings in the naphthalene, anthracene, and similar systems.

The numbering begins at the top of the ring on the extreme right (that is, the atom in the ortho-position to the second ring), and each atom of the first ring is numbered before proceeding to the second ring; for example:


Naphthalene.


Phenanthrene.

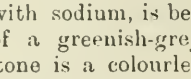

Acridine.

[This re-numbering is not followed in the abstract.]

Hydroxymethylene*cyclo*hexanone (Wallach, Abstr., 1904, i, 105) is best prepared by the action of sodium wire on a mixture of *cyclo*hexanone and *iso*amyl formate. It has b. p. 87°/14 mm., and tends to resinify when kept. With aniline, it yields *α-ketohexahydrobenzylidene aniline*, $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CO\end{matrix}>CH\cdot CH{:}NPh$, which crystallises from alcohol in yellow needles, m. p. 154°. Heating with concentrated sulphuric acid transforms this compound into *α-ketohexahydrobenzylideneaniline-p-sulphonic acid*, $C_{13}H_{15}O_4NS$, which can also be obtained by condensing hydroxymethylene*cyclo*hexanone with aniline-*p*-sulphonic acid in the presence of *N*-potassium hydroxide. It forms yellow needles, m. p. 261—262°, yields an *ammonium* salt in the form of yellow plates, and a *potassium* salt in the form of rhombic crystals, m. p. 269—270° (decomp.).

α-Ketohexahydrobenzylidene-m-*aminophenol*, $C_{13}H_{15}O_2N$, prepared by condensing the components in glacial acetic acid solution, crystallises in yellow needles, m. p. 172—173°. Neither of the above condensation products yields a quinoline derivative.

*Acetyl*cyclo*hexan-2-one*, $CH_2<\begin{matrix}CH_2\text{--}CO\\CH_2\text{-}CH_2\end{matrix}>CHAc$, prepared by the condensation of *cyclo*hexanone and ethyl acetate with sodium, is best isolated as its *copper* derivative in the form of a greenish-grey, crystalline powder, m. p. 160—161°. The free ketone is a colourless oil with b. p. 97—98°/11 mm., and can be kept for some time. It condenses with *m*-aminophenol in glacial acetic acid solution, yielding the m-*hydroxyanil*, $OH\cdot C_6H_4\cdot N{:}C_6H_9Ac$, as yellow needles, m. p. 186—187°, which react with concentrated sulphuric acid at 100°, yielding the quinoline derivative, 5-*methyl*-8-*hydroxy*-1:2:3:4-*tetrahydroacridine* (5-*methyl*-7-*hydroxy*-2:3-*hexamethylenequinoline*: annexed formula). The *sulphate* crystallises from dilute alcohol in yellowish-white needles, m. p. 225°, and the free base crystallises in glistening plates, which darken at 240°, but are not completely molten at 360°; its solutions have a yellowish-green fluorescence.

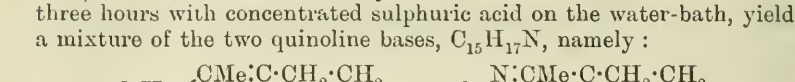


Aniline and *d*-4-acetyl-1-methyl*cyclo*hexan-3-one react at 150°, yielding a mixture of isomeric anils, $COMe\cdot C_6H_8Me{:}NPh$ and

$OH\cdot C_6H_7Me\cdot CMe{:}NPh$,

or the tautomeric enolic forms. A mixture of the two has b. p.

211°/14 mm., and cannot be separated; the mixture, when heated for three hours with concentrated sulphuric acid on the water-bath, yields a mixture of the two quinoline bases, $C_{15}H_{17}N$, namely:



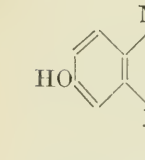
d-2 : 5-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroacridine*. and d-6 : 9-*Dimethyl*-5 : 6 : 7 : 8-*tetrahydrophenanthridine*.

A mixture of the two has b. p. 200°/14 mm., and the separation is based on the fact that the former yields a sparingly soluble hydrochloride and the latter a sparingly soluble dichromate. The acridine base crystallises from light petroleum in colourless needles, m. p. 72—74°, and $[\alpha]_D$ +57·07°. Its solutions in acids have a greenish-yellow fluorescence. The *picrate* forms a yellow, crystalline powder, m. p. 193°; the *methiodide*, $C_{16}H_{20}NI$, crystallises from alcohol in yellow needles, m. p. 232—233°; the *platinichloride*,

$$2C_{15}H_{17}N_2,H_2PtCl_6,$$

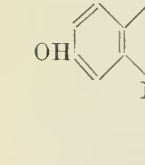
forms orange-coloured needles, m. p. 213—223°, and the *aurichloride*, $2C_{15}H_{18}NCl,AuCl_3$, yellow needles, m. p. 166°. The same base can also be prepared by condensing *o*-aminoacetophenone with *d*-3-methyl-*cyclo*hexanone, and when distilled with zinc dust in an atmosphere of hydrogen yields 2 : 5-*dimethylacridine*, $C_{15}H_{13}N$, colourless needles, m. p. 121—122°, the *picrate* of which is sparingly soluble in hot alcohol and has m. p. 225°. A by-product is 2 : 5-*dimethyl*-5 : 10-*dihydroacridine*, $C_{15}H_{15}N$, which crystallises from alcohol in colourless plates, m. p. 165—166°.

The dimethyltetrahydrophenanthridene crystallises from light petroleum, has m. p. 78° and $[\alpha]_D$ +133·7°, and its solutions in acids do not fluoresce. The *picrate* has m. p. 208° (decomp.); the *aurichloride*, $C_{15}H_{17}N,HAuCl_4$, crystallises in yellow needles, m. p. 128°. 9 : 10-*Dimethylphenanthridene*, $C_{15}H_{13}N$, is a colourless oil, and yields a *picrate*, m. p. 214°.



(I.)

d-1-*Methyl*-4-*acetyl*cyclo*hexan*-3-*one*-m-*hydroxyanil*, OH·CMe:C_6H_7Me:N·C_6H_4·OH, obtained from *m*-aminophenol and *d*-1-methyl-4-acetyl*cyclo*hexan-3-one, separates from alcohol in yellow, crystalline aggregates, m. p. 153—154°, and with sulphuric acid yields 2 : 5-*dimethyl*-8-*hydroxy*-1 : 2 : 3 : 4-*tetrahydroacridine* (formula I). This forms greenish-yellow crystals, m. p. 272—273°, and yields a *sulphate* in the form of colourless needles, m. p. 207—208°. When distilled with zinc dust in an atmosphere of hydrogen, the base yields 2 : 5-dimethylacridine.



(II.)

d-*α*-*Acetylcamphor*-m-*hydroxyanil*, $C_{10}H_{15}$Ac:N·C_6H_4·OH,] crystallises from alcohol in colourless, flat needles, m. p. 151—152°, and with concentrated sulphuric acid yields the quinoline *base*, $C_{18}H_{21}ON$ (formula II). This crystallises in yellow needles, which are unaltered at 360°, and yields a *picrate*.

1 : 2 : 3 : 4-*Tetrahydroacridine*-5-*carboxylic acid*,

$$C_6H_4<\begin{matrix}C(CO_2H)\\ \\ N\end{matrix}>C_6H_8,$$

prepared by condensing *cyclo*hexanone with isatin in the presence of 33% potassium hydroxide and alcohol, crystallises in colourless, glistening plates, m. p. 284—286° (decomp.). The *picrate* forms yellow needles, m. p. 199·5° (decomp.); the *aurichloride*,

$$(C_{14}H_{13}O_2N,HCl)_3,2AuCl_3,10H_2O,$$

has m. p. 237° (decomp.); the *platinichloride*,

$$2C_{14}H_{13}O_2N,H_2PtCl_6,6H_2O,$$

forms glistening, brown crystals, m. p. 222—223°; and the *methyl* ester, $C_{13}H_{12}N\cdot CO_2Me$, prepared from the silver salt, has b. p. 200°/20 mm. and m. p. 70°; it yields a *picrate*, m. p. 176—178°, and a *platinichloride*, as red needles, m. p. 204—208°; the *ethyl* ester,

$$C_{13}H_{12}N\cdot CO_2Et,$$

forms broad needles, m. p. 55°, and yields a *picrate*, m. p. 166—167°, a *platinichloride*, $2C_{16}H_{17}O_2N,H_2PtCl_6$, m. p. 193—194°, and an *ethiodide*, $C_{18}H_{22}O_2NI$, m. p. 168°. 1 : 2 : 3 : 4-Tetrahydroacridine, prepared by heating the carboxylic acid at its m. p., yields a *sulphate*, with m. p. 148°, and a *mercurichloride*, in the form of colourless needles, m. p. 213—214°. The base condenses with benzaldehyde and zinc chloride at 160—170°, yielding 1-*benzylidene*-1 : 2 : 3 : 4-*tetrahydroacridine*, $C_6H_4<\begin{matrix}C=C\cdot CH_2\\ |\\ N=C\cdot C(:CHPh)\cdot CH_2\end{matrix}>\begin{matrix}---CH_2\\ |\\ \end{matrix}$, which crystallises from dilute alcohol in glistening plates, m. p. 103—104°. Its *picrate* has m. p. 176—178°. Tetrahydroacridine and phthalic anhydride yield a *phthalone*. When nitrated with 10% nitric acid, the tetrahydro-base yields a mixture of two *nitro*-derivatives, $C_{13}H_{12}N\cdot NO_2$, namely, dark yellow prisms, melting at 126—130°, and yellow needles, m. p. 138—139°, which have to be separated mechanically. With fuming sulphuric acid at 100°, the base yields *tetrahydroacridine*-6-*sulphonic acid*, $C_{13}H_{13}O_3NS$, which crystallises from water in colourless prisms, but at 130—140° the chief product is an isomeric *sulphonic acid*, m. p. 248—250°, together with a small amount of the above sulphonic acid, which is not molten at 300°, and of a *disulphonic acid*.

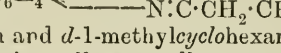
The base reacts with bromine, yielding the *hydrobromide perbromide* $C_{13}H_{13}N,HBr_3$, as yellowish-red needles, m. p. 123°.

7-*Bromo*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*,

$$C_6H_3Br<\begin{matrix}C(CO_2H)\\ \\ N\end{matrix}>C_6H_8,$$

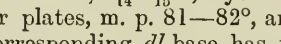
prepared from *cyclo*hexanone, 5-bromoisatin, and alkali, crystallises in minute needles, m. p. 274—276°, after drying at 120°. When heated at its m. p., the acid yields 7-*bromotetrahydroacridine*, $C_{13}H_{12}NBr$ which crystallises from alcohol in flat needles, m. p. 93—94°. The *picrate* crystallises in greenish-yellow plates, m. p. 194—195°, and the *aurichloride* in microscopic needles, m. p. 208°. 7 : 9-*Dibromo*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*, $C_{14}H_{11}O_2NBr_2$, prepared from 3 : 5-dibromoisatin, crystallises in broad needles, m. p. 242°. 7 : 9-*Dibromotetrahydroacridine*, $C_{13}H_{11}NBr_2$, crystallises in yellow needles, m. p. 105—107°.

d-2-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*,



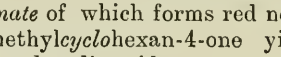
obtained from isatin and *d*-1-methyl*cyclo*hexan-3-one, crystallises from glacial acetic acid in yellow needles, m. p. 291—293° (decomp.). d-2-*Methyltetrahydroacridine*, $C_{14}H_{15}N$, crystallises from light petroleum in colourless, slender plates, m. p. 81—82°, and yields a *picrate*, m. p. 176—177°. The corresponding *dl*-base has m. p. 72—73°, and both the *d*- and the *dl*-base when heated with lead oxide yield 3-methylacridine, the *dichromate* of which forms red needles, m. p. 125—126°.

Isatin and 1-methyl*cyclo*hexan-4-one yield 3-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*,



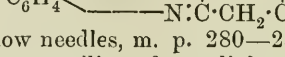
in the form of yellow needles, m. p. 280—281°. 3-*Methyltetrahydroacridine*, $C_{14}H_{15}N$, crystallises from light petroleum in quadratic plates, m. p. 84—85°, and yields a *picrate*, m. p. 194—195°. When heated with lead oxide, the base yields 3-methylacridine (Ullmann, Abstr., 1888, 288).

Pulegone and isatin in the presence of concentrated potassium hydroxide yield α-methylcinchonic acid, together with neutral products, probably owing to the conversion of the pulegone into acetone and 1-methyl*cyclo*hexan-3-one.

2 : 3-*Trimethylenecinchonic acid*, 

obtained from isatin, *cyclo*pentanone, and alkali, crystallises from alcohol or glacial acetic acid in small needles, m. p. 277—278° (decomp.). 2 : 3-*Trimethylenequinoline*, $C_{12}H_{11}N$, formed when the acid is heated at its m. p. or by condensing *cyclo*pentanone with *o*-aminobenzaldehyde, crystallises from light petroleum in colourless needles, m. p. 59—60°; the *dichromate* forms sparingly soluble, orange, yellow prisms; the *picrate*, pale yellow needles, m. p. 203—204°; the *aurichloride*, $C_{12}H_{11}N,HAuCl_4$, needles, m. p. 160—162°; the *platinichloride*, reddish-yellow needles, m. p. 235°; and the *methiodide*, $C_{13}H_{14}NI$, pale yellow crystals, m. p. 207°.

2 : 3-*Pentamethylenecinchonic acid*,



crystallises from glacial acetic acid in glistening needles, m. p. 291—292°, and 2 : 3-*pentamethylenequinoline*, $C_{14}H_{15}N$, from light petroleum in colourless needles, m. p. 93·5°; its *hydrochloride* forms broad needles, m. p. 107—108°; its *picrate*, yellow needles, m. p. 197°; its *methiodide* has m. p. 195—196°; its *aurichloride*,

$$C_{14}H_{15}N,HAuCl_4,$$

forms yellow needles, m. p. 179°, and its *platinichloride* crystallises with $2H_2O$ in orange-red needles, m. p. 214°. J. J. S.

Oxazole Series. Syntheses of 2-Ketotetrahydro-oxazoles. Treat B. Johnson and Ralph W. Langley (*Amer. Chem. J.*, 1910, 44, 352—361).—Nemirowsky (Abstr., 1885, 741) has shown that

carbonyl chloride reacts with β-chloroethyl alcohol at 200° to form β-chloroethyl chloroformate. When this ester was treated with aniline, chloroethyl phenylcarbamate, $CH_2Cl\cdot CH_2\cdot O\cdot CO\cdot NHPh$, was produced, and was converted by alkali hydroxide into 2-keto-3-phenyltetrahydro-oxazole, $O<\begin{matrix}CO-NPh\\ |\\ CH_2\cdot CH_2\end{matrix}$. Otto (Abstr., 1891, 1373) studied the action of carbonyl chloride on the dichlorohydrins, and obtained acid chlorides, from which he prepared a series of urethanes. He found that the urethanes from αα-dichlorohydrin yielded ketotetrahydro-oxazoles when they were treated with alkali hydroxide, whilst those from αβ-dichlorohydrin did not behave in this way. In view of these results, a study has now been made of various halogenalkyl phenylcarbamates and their behaviour towards alkali hydroxide.

ββ-Dichloroisopropyl phenylcarbamate, $CH(CH_2Cl)_2\cdot O\cdot CO\cdot NHPh$, m. p. 73°, obtained by the action of phenylcarbimide on αα-dichlorohydrin at 100°, crystallises in groups of slender needles, and when heated with potassium hydroxide is converted almost quantitatively into 2-keto-3-phenyl-5-chloromethyltetrahydro-oxazole,

$$O<\begin{matrix}CO-\!-\!-\!-NPh\\ |\\ CH(CH_2Cl)\cdot CH_2\end{matrix}$$

(Otto, *loc. cit.*).

ββ′-Chlorobromoisopropyl phenylcarbamate, m. p. 73°, obtained by the interaction of phenylcarbimide and ββ′-chlorobromo*iso*propyl alcohol, crystallises in needles, and is converted by potassium hydroxide into 2-keto-3-phenyl-5-chloromethyltetrahydro-oxazole.

β-Chloro-γ-bromopropyl phenylcarbamate, m. p. 73°, was prepared from phenylcarbimide and β-chloro-γ-bromopropyl alcohol. *γ-Chloro-β-bromopropyl phenylcarbamate*, m. p. 75—76°, is converted by potassium hydroxide into *2-keto-3-phenyl-4-chloromethyltetrahydro oxazole*,

$$O<\begin{matrix}CO-NPh\\ |\\ CH_2\cdot CH(CH_2Cl)'\end{matrix}$$

m. p. 73—78°, which forms groups of needles. A small yield of this oxazole was also obtained by the action of potassium hydroxide on ββ′-dichloropropyl phenylcarbamate. *ββ′-Dibromoisopropyl*, *βγ-dichloropropyl*, and *βγ-dibromopropyl phenylcarbamates* have m. p. 73°, 72—73°, and 77—79° respectively. E. G.

Oxazole Series: the Addition of Cyanic Acid to Epichlorohydrin. Treat B. Johnson and Herbert H. Guest (*Amer. Chem. J.*, 1910, **44**, 5, 453—466).—Thomsen (Abstr., 1879, i, 217) has described the formation of a ketotetrahydro-oxazole, $C_4H_6O_2NCl$, from the action of potassium cyanate on epichlorohydrin. The authors have synthesised this substance by the action of strong alkali on ββ′-dichloro*iso*propyl acetylcarbamate, and thus determined the manner of addition of cyanic acid to epichlorohydrin. It is shown that theoretically three isomeric cyclic compounds might be formed by this addition: 2-keto-5-chloromethyltetrahydro-oxazole, 2-keto-4-chloromethyltetrahydro-oxazole, and γ-chloropropylene iminocarbonate, and that the substance formed must be assigned the structure of the first of these.

ββ'-Dichloroisopropyl acetylcarbamate, $NHAc\cdot CO_2\cdot CH(CH_2Cl)_2$, crystallises in needles, m. p. 100°.

ββ'-Dichloroisopropyl benzoylcarbamate crystallises in rectangular prisms, m. p. 119°. *2-Keto-3-phenylcarbamyl-5-chloromethyltetrahydro-oxazole*, $CH_2Cl\cdot CH<\begin{matrix}O—CO\\ |\\ CH_2\cdot N\cdot CO\cdot NHPh\end{matrix}$, forms rhombic tablets, m. p. 154—155°; the corresponding *3-benzoylcarbamyl* derivative melts at 131—132°.

β-γ-Dichloropropyl acetylcarbamate forms prisms, m. p. 64—65°.

Allyl acetylcarbamate crystallises in flat prisms, m. p. 64°.

γ-Chloro-β-bromopropyl acetylcarbamate crystallises in prisms, m. p. 60°. *γ-Chloro-β-bromopropyl carbamate* forms plates, m. p. 93°. *β-β'-Dibromoisopropyl benzoylcarbamate* crystallises in plates, m. p. 119°; the *β-chloro-β-bromo*-derivative melts at 122°.

β-γ-Dichloropropyl benzoylcarbamate and the corresponding *dibromo*-derivative melt at 83°.

γ-Chloro-β-bromopropyl benzoylcarbamate forms tabular crystals, m. p. 113°.

β-Chloro-γ-bromopropyl benzoylcarbamate crystallises in prisms, m. p. 114°. N. C.

Diphenylene-sultam. Fritz Ullmann and Christian Gross (*Ber.*, 1910, **43**, 2694—2704).—A sultam could not be obtained from toluene-*p*-sulpho-3-nitro-*p*-toluidide, but one was prepared from *o*-nitrobenzenesulphonanilide, the reduction product of which,

$$NH_2\cdot C_6H_4\cdot SO_2\cdot NHPh,$$

was diazotised, and on the addition of sodium acetate formed *1-phenyl-benzsulphontriazine*, $C_6H_4<\begin{matrix}SO_2\cdot NPh\\ |\\ N=N\end{matrix}$; this was converted by sodium hydroxide and copper into *diphenylene-sultam*,

$$C_6H_4<\begin{matrix}SO_2\\ C_6H_4\end{matrix}>NH.$$

Phenylenenaphthylene-sultam was prepared in a similar manner. Both sultams are colourless, crystalline compounds of strongly acid character. The ring is not opened on heating with hydrochloric acid even under pressure.

Nitro-p-*toluenesulphonyl*-3 : 5-*dinitro*-p-*toluidide*, prepared by nitration of *p*-toluenesulphonyl-*p*-toluidide, crystallises in colourless prisms, m. p. 184°. Sulphuric acid converts it into 3 : 5-dinitro-*p*-toluidine. With methyl sulphate, p-*toluenesulphonylmethyl*-3 : 5-*dinitro*-p-*toluidide* is formed in faintly yellow crystals, m. p. 199°.

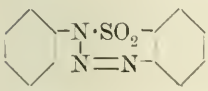
p-*Toluenesulphonyl*-3-*nitro*-p-*toluidide*, produced on nitrating with 18% nitric acid at 60—70°, forms yellow prisms, m. p. 101°. It yields 3-nitro-*p*-toluidine when hydrolysed. When reduced with stannous chloride, p-*toluenesulphonyltolylene*-3 : 4-*diamine* is obtained; it crystallises in needles, m. p. 140°; the *hydrochloride* forms colourless, silky needles, decomp. 170°. p-*Toluenesulphonylaziminotoluene* forms colourless needles, m. p. 159°. p-*Toluenesulphonylmethyl*-3-*nitro*-p-*toluidide* has m. p. 124°. p-*Toluene sulphonylmethyl*-3-*amino*-p-*toluidide* forms colourless, matted needles, m. p. 133°.

Di-p-*toluenesulphonyl*-3-*nitro*-p-*toluidide* forms colourless needles, m. p. 228°; reduction converts it into *di*-p-*toluenesulphonyl*-*tolylene diamine*, crystallising in colourless needles, m. p. 192°.

o-*Nitrobenzenesulphonanilide* has m. p. 115°; o-*aminobenzenesulphonanilide* forms matted needles, m. p. 122°; the *hydrochloride* separates in colourless needles.

Diphenylene-sultam crystallises in well-formed, colourless, lustrous needles, m. p. 196°; it dissolves in ammonia and alkalis with a faint yellow coloration and bluish fluorescence. The mother liquors of the preparation contain *hydroxybenzenesulphonanilide*, colourless needles, m. p. 123°.

1-*Phenylbenzsulphontriazine* (annexed formula) is amorphous, m. p. 111° (decomp.). The triazine ring is immediately opened by dilute mineral acids, and the clear solutions couple with β-naphthol, forming red azo-dyes.



Diphenylene-N-*methylsultam* is obtained from *nitrobenzene sulphonmethylanilide*, m. p. 73°, which is reduced by stannous chloride to *aminobenzenesulphonmethylanilide*, forming colourless crystals, m. p. 63°. The last substance when diazotised, and the diazonium solution evaporated, gives the *sultam* in colourless needles, m. p. 112°.

o-*Nitrobenzenesulphonyl*-β-*naphthalide* forms colourless needles, m. p. 138°; on reduction, o-*aminobenzenesulphonyl*-β-*naphthalide* is formed, crystallising in needles, m. p. 113°.

1-β-*Naphthyl-benzsulphontriazine*, $C_6H_4\begin{cases}N{=}N\\ SO_2{\cdot}N{\cdot}C_{10}H_7\end{cases}$, separates in colourless needles, m. p. 107—108°.

Phenylenenaphthalene-sultam, $C_6H_4\begin{cases}SO_2\\ C_{10}H_6\end{cases}NH$, crystallises in colourless needles, m. p. 254°; the solutions fluoresce faintly blue.

E. F. A.

Isomerism of Complex Compounds. I. Asymmetric Complex Compounds of Platinum. Iwan Ostromisslensky and August Bergmann (*Ber.*, 1910, **43**, 2768—2774; *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 611—624).—The object of the authors was to prepare complex compounds of platinum of the type $\begin{matrix}a\\b\end{matrix}\!\!>\!Pt\!<\!\!\begin{matrix}m\\n\end{matrix}$ or $\left[\begin{matrix}a\\b\end{matrix}\!\!>\!Pt\!<\!\!\begin{matrix}m\\n\end{matrix}\right]m_2$ in order to see if optical isomerides are capable of existence. If this were so it would follow that Werner's explanation of the existence of two isomerides of the formula $Cl_2Pt(NH_3)_2$ is not a correct one. The stable, asymmetric compound, cis-*plato-pyridine-ammine-chlorosulphite*, $\begin{matrix}Cl\\ HO_3S\end{matrix}\!\!>\!Pt\!<\!\!\begin{matrix}NH_3\\ NC_5H_5\end{matrix}$, has been prepared, but so far no evidence of isomerism has been obtained.

To prepare the above compound, sulphur dioxide is passed into an aqueous suspension of plato-semipyridine-ammine-chloride (Abstr., 1886, 857) heated on the water-bath. The ammine-chloride dissolves, leaving undissolved a small quantity of a yellow substance (*A*). The filtrate, on concentration, gives clear, colourless, monoclinic crystals

[$a:b:c=0{\cdot}966:1:0{\cdot}712$; $\beta=91°43'$] of the plato-pyridine-ammine-chlorosulphite. With brucine it gives an easily soluble salt or double compound.

The mother liquors from the chlorosulphite sometimes deposit a yellow substance, which is identical with *A*. It is soluble in chloroform, and can thus be separated from the chlorosulphite, which is practically insoluble. It contains the same percentage of platinum and nitrogen as the chlorosulphite, but it is not isomeric or identical with it, as it does not contain sulphur. A formula is not given for it.

Plato-semitolylenediamine chloride, $[Cl_2Pt(NH_2)_2{\cdot}C_6H_3{\cdot}CH_3]$, was obtained by warming potassium platinochloride with 1 : 3 : 4-tolylenediamine. It forms microscopic, yellow needles, with a green tinge, which are insoluble in ordinary solvents. Attempts to prepare an asymmetric complex from it by replacing one of the chlorine atoms by the SO_3H group were not successful. Treatment with sulphites, bisulphites, or sulphur dioxide gave precipitates which were analysed, but to which the authors assign no formula.

Plato-semi*iso*butylenediamine chloride, as also the asymmetric compound, $\left[\begin{matrix}H_2C{\cdot}NH_2\\ |\\ Me_2C{\cdot}NH_2\end{matrix}\!\!>\!Pt(NH_2)_2{\cdot}C_6H_3CH_3\right]$, are not capable of existence.

T. S. P.

Nitrosohydrazines, *iso*Azotates [*iso*Diazo-compounds], and Azo-compounds of the Aliphatic Series. Johannes Thiele (*Annalen*, 1910, **376**, 239—268; Abstr., 1908, i, 927).—The main object of the paper is to show that aliphatic *iso*azotates (*iso*diazo-compounds) behave like their aromatic analogues, except, of course, that they do not yield diazonium salts with acids.

The production of *iso*diazo-compounds from a primary hydrazine (or its nitroso-derivative, which has an asymmetric structure), ethyl nitrite, and sodium ethoxide is represented by the scheme: $NHR{\cdot}NH_2 \longrightarrow N(NO)R{\cdot}NH_2 \longrightarrow N(NO)R{\cdot}NH{\cdot}NO \longrightarrow N_2O+NHR{\cdot}NO$ (a decomposition resembling that of *sec.-as*-hydrazines by nitrous acid) $\longrightarrow RN{:}N{\cdot}ONa$. (The formation of Hantzsch and Lehmann's azotates, which are quite different from the *iso*azotates, from nitrosoalkylurethanes and very concentrated potassium hydroxide is explained by the intermediate formation of the same primary nitrosoamine, NHR·NO. Further research is necessary in order to explain the remarkable difference in the course of the two reactions.)

Methylhydrazine sulphate, which is conveniently prepared by heating a benzene solution of benzylideneazine with methyl sulphate for five hours and decomposing the additive product with water, is exactly neutralised by sodium hydroxide, and the solution is treated with three times the calculated amount of 5*N*-nitrite and is made distinctly acid with acetic acid; when the mixture becomes neutral, acetic acid is again added, and so on for about eight hours until the methylhydrazine has been converted into *nitrosomethylhydrazine*, $NO{\cdot}NMe{\cdot}NH_2$, m. p. 45°, which is then liberated by sodium carbonate and extracted with ether. Its aqueous solution develops an intense violet coloration with ferric chloride, yields a white precipitate with

mercuric salts, and gives a reddish-brown, crystalline precipitate, and ultimately a reddish-brown coloration, with copper sulphate after the addition of sodium acetate or hydroxide. It reacts with an aqueous suspension of benzaldehyde containing a trace of sulphuric acid to form *nitrosobenzylidenemethylhydrazine*, $CHPh{:}N{\cdot}NMe{\cdot}NO$, m. p. 77—78°, with 10% sodium hydroxide and benzoyl chloride to form *benzoylnitrosomethylhydrazine*, $NHBz{\cdot}NMe{\cdot}NO$, m. p. 126—127° (decomp., rapidly heated), and with *N*/2-sodium hydroxide and benzenesulphonyl chloride to form *benzenesulphonylnitrosomethylhydrazine*, $SO_2Ph{\cdot}NH{\cdot}NMe{\cdot}NO$, m. p. 83°; the last two compounds, like the corresponding *derivatives* of nitrosobenzylhydrazine,

$$NHBz{\cdot}N(NO){\cdot}CH_2Ph,$$

m. p. 126—127°, and $SO_2Ph{\cdot}NH{\cdot}N(NO){\cdot}CH_2Ph$, m. p. 115—116°, do not develop a violet coloration with ferric chloride.

In methylhydrazine the nitrogen atom which is already alkylated is alone attacked by further methylation. Nitrosomethylhydrazine and nitrosobenzylhydrazine, however, readily react with methyl sulphate or benzyl chloride in the presence of aqueous sodium hydroxide, yielding *nitrosohydrazomethane*, $NHMe{\cdot}NMe{\cdot}NO$, b. p. 56°/10 mm., *nitroso-αβ-dibenzylhydrazine*, $CH_2Ph{\cdot}NH{\cdot}N(NO){\cdot}CH_2Ph$, m. p. 69°, *α-nitroso-β-benzyl-α-methylhydrazine*, $CH_2Ph{\cdot}NH{\cdot}NMe{\cdot}NO$, m. p. 53°, and *α-nitroso-α-benzyl-β-methylhydrazine*, $NHMe{\cdot}N(NO){\cdot}CH_2Ph$, m. p. 39°, all of which give intense blue colorations with ferric chloride instead of the violet colorations obtained with monoalkylated nitrosohydrazines. Since the group $\cdot N{:}N{\cdot}OH$ cannot be present in these four dialkylated nitrosohydrazines, it follows that this group is also not present in monoalkylated nitrosohydrazines, which therefore cannot have the symmetrical structure $NHR{\cdot}NH{\cdot}NO$, in which alone tautomerisation could occur in such a way as to form the group $\cdot N{:}N{\cdot}OH$. α-Nitroso-β-benzyl-α-methylhydrazine and α-nitroso-α-benzyl-β-methylhydrazine exhibit very similar properties, but they depress each other's m. p., and the latter is changed into the former by mineral acids; the two substances are not identical, and consequently nitrosodialkylhydrazines cannot have the constitution $OH{\cdot}N{<}^{NR}_{NR'}$.

Fission into an amine and nitrogen monoxide has been accomplished hitherto only in nitrosohydrazines of the aromatic series. Now it is shown that members of the aliphatic series decompose in a similar manner, by heating nitrosobenzylhydrazine with ethyl oxalate; the resulting amine is isolated partly as *benzyloxamide*, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_7H_7$, m. p. 223°, mainly as *ethyl benzyloxamate*, $CO_2Et{\cdot}CO{\cdot}NH{\cdot}C_7H_7$, m. p. 48°.

Sodium methylisoazoxide, $NMe{:}N{\cdot}ONa$, is obtained in slender, white needles by treating methyl-alcoholic nitrosomethylhydrazine with sodium methoxide, ether, and ethyl nitrite; it inflames when heated or when treated with concentrated sulphuric acid, explodes in moist carbon dioxide, yields diazomethane when heated at 130—200°/12 mm., gives in aqueous or alcoholic solution a characteristic reddish-violet coloration with copper acetate, is reduced to methylhydrazine by 8—10% sodium hydroxide and aluminium, and is oxidised to methylnitroamine

by alkaline potassium ferricyanide. The *iso*diazomethane liberated from the sodium salt changes at once to diazomethane; thus, ordinary acids cause an evolution of nitrogen, benzoic acid produces methyl benzoate, hydrogen cyanide produces methylcarbylamine, and β-naphthol produces β-naphthyl methyl ether. Sodium benzyl*iso*azoxide (*loc. cit.*) is unstable, decomposes in carbon dioxide, yields benzyl alcohol with dilute sulphuric acid, and benzyl β-naphthyl ether with β-naphthol, is reduced to benzylhydrazine by aluminium and 8% sodium hydroxide, and is oxidised by alkaline potassium ferricyanide to *benzylnitroamine*, $CH_2Ph{\cdot}NH{\cdot}NO_2$, m. p. 38—39°, which forms a mercury *derivative*, $Hg(C_7H_7O_2N_2)_2$.

s-Dibenzylhydrazine is best prepared by the cathodic reduction of a methyl-alcoholic solution of benzylideneazine containing potassium hydroxide; its dinitroso-derivative has m. p. 44°, and yields *s*-diphenylazomethane when gently warmed in the absence of air. *s-Benzylmethylhydrazine dihydrochloride*, $NHMe{\cdot}NH{\cdot}CH_2Ph,2HCl$, m. p. 140° (decomp.), is obtained by boiling either of the nitrosobenzylmethylhydrazines with concentrated hydrochloric acid.

s-Diphenylazomethane (*ω-azotoluene*), $CH_2Ph{\cdot}N{:}N{\cdot}CH_2Ph$, m. p. 31·5°, is obtained by oxidising *s*-dibenzylhydrazine by 3% hydrogen peroxide and 20% ammonium hydroxide; it crystallises in colourless leaflets, and in alcoholic solution is converted into benzylidenebenzylhydrazone by a few drops of hydrochloric acid. In a similar manner, *s*-phenylbenzylhydrazine is oxidised to *benzeneazophenylmethane*, $NPh{:}N{\cdot}CH_2Ph$, an orange-coloured oil which readily changes to benzaldehydephenylhydrazone, slowly at the ordinary temperature, rapidly at 200°. C. S.

Formation of Hydrazones. Ugo Grassi (*Gazzetta*, 1910, **40**, ii, 139—153).—The formation of menthonephenylhydrazone from menthone and phenylhydrazine in ethyl-alcoholic solution is complete; it is unimolecular, and the velocity is proportional to the quantity of acid present. In methyl alcohol the velocity is less. The formation of camphorphenylhydrazone could not be followed by the polarimetric method employed for the menthone derivative, but it was found possible to obtain indications that the reaction proceeds three hundred times more slowly than in the case of the latter, when the concentration of acid is the same.

A formula is worked out for the determination of reaction constants based on the measurement of the partition of the phenylhydrazine between two ketones, of which one is optically active. In the case of methyl propyl ketone, methyl *iso*propyl ketone, and pinacolin, compared in this way with menthone, the following relative reaction constants (K_2/K_1) were found respectively: 5·3, 2·71, 1·29. It follows that the branching of the carbon chain diminishes the readiness of formation of hydrazones.

The author has devised another method founded on the fact that the conductivity of an alcoholic solution of phenylhydrazine and an acid diminishes when phenylhydrazine is withdrawn from the liquid, so that from conductivity measurements it is possible to calculate the quantity of phenylhydrazine remaining in the solution at any time. The solu-

tions employed were 0·022*N* as regards the phenylhydrazino and the ketones, with 0·0065*N*-salicylic acid, and the observed conductivity ranged from 393 (initial) to 43 (final). The following are the reaction constants for the formation of phenylhydrazones of various ketones, the reactions being in all cases complete and unimolecular in the earlier stages: acetone, 0·122; methyl propyl ketone, 0·0228; methyl *iso*-propyl ketone, 0·0114; pinacolin, 0·0043; benzaldehyde, 0·35; salicylaldehyde, 0·416; *m*-hydroxybenzaldehyde, 0·194; *p*-hydroxybenzaldehyde, 0·025; anisaldehyde, 0·061; protocatechualdehyde, 0·019; protocatechualdehyde carbonate, 0·123; piperonaldehyde, 0·048; vanillin, 0·060; *iso*vanillin, 0·048. Owing to the rapidity of the reactions, it was necessary to carry out the measurements at 10°. A simple thermostat is described convenient for this purpose, the low temperature being maintained by a supply of ice-water controlled by an electric thermoregulator. R. V. S.

Derivatives of α-Amino-*n*-butyric Acid. Arnold Hildesheimer (*Ber.*, 1910, **43**, 2796—2805).—*α-Phthalimino*-n-*butyric acid*,

$$C_8H_4O_2{:}N{\cdot}CHEt{\cdot}CO_2H,$$

is readily formed when the corresponding ester (Gabriel and Colman, Abstr., 1900, i, 359) is warmed with concentrated sulphuric acid for some three-quarters of an hour, and the mixture poured on to ice. It forms a resinous mass, which can be obtained in a crystalline form only with great difficulty, and then has m. p. 94—95°. The acid reacts with phosphorus pentachloride, yielding the corresponding acid chloride, which condenses with benzene in the presence of aluminium chloride, forming *phenyl phthaliminopropyl ketone*,

$$C_8H_4O_2{:}N{\cdot}CHEt{\cdot}COPh.$$

The ketone crystallises from light petroleum in colourless, six-sided plates, m. p. 118°, and on hydrolysis with hydrochloric acid yields *phenyl α-aminopropyl ketone hydrochloride*, $NH_2{\cdot}CHEt{\cdot}COPh,HCl$, m. p. 178° after sintering at 170°. The *picrate* has m. p. 174° after sintering at 160°, and the *platinichloride* has m. p. 190—200° (decomp.).

3 : 6-*Diphenyl*-2 : 5-*diethyl*-2 : 5-*dihydropyrazine*,

$$CPh\lessdot\begin{matrix}N{\cdot}CHEt\\CHEt{\cdot}N\end{matrix}\gtrdot CPh,$$

is formed when an aqueous solution of phenyl aminopropyl ketone hydrochloride is mixed with ammonium hydroxide solution, the flask completely filled with air-free water, corked, and kept overnight. The *hydrochloride*, $C_{20}H_{23}N_2Cl$, forms a red, crystalline mass, m. p. 167—168° (decomp.).

The base and its hydrochloride are readily oxidised, even on exposure to the air; with dilute nitric acid, oxidation is instantaneous, and the product is Collet's 3 : 6-diphenyl-2 : 5-diethylpyrazine. On hydrolysis with hydrochloric acid in an atmosphere of carbon dioxide, the dihydro-base yields mainly phenyl α-aminopropyl ketone, with probably a small amount of the isomeric ketone, $NH_2{\cdot}CHPh{\cdot}COEt$ (compare Gabriel, Abstr., 1908, i, 466).

Potassium thiocyanate reacts with an aqueous solution of phenyl aminopropyl ketone hydrochloride, yielding 2-*thiol*-5(or 4)-*phenyl*-4

(or 5)-*ethylglyoxaline*, $\begin{matrix}CPh\cdot NH\\ \|\\ CEt{-}N\end{matrix}\!\!>C\cdot SH$ or $\begin{matrix}CPh{-}N\\ \|\\ CEt\cdot NH\end{matrix}\!\!>C\cdot SH$, in the form of snow-white needles, m. p. 272° after changing colour at 260°. Nitric acid oxidises the thiol to *αβ*-phenylethylthiazole, $C_{11}H_{12}N_2$, m. p. 172°.

α-Phthaliminobutyric acid reacts with red phosphorus and bromine (compare Gabriel, Abstr., 1908, i, 182), yielding *αβ-dibromo-α-phthaliminopropane*, $C_8H_8O_2{:}N\cdot CHBr\cdot CHMeBr$, which crystallises from alcohol in well-developed octahedra, m. p. 147°. When boiled for an hour with water, the bromo-derivative yields phthalimide, hydrogen bromide (1 mol.), and α-bromopropaldehyde according to the equation: $C_8H_4O_2{:}N\cdot CHBr\cdot CHBrMe + H_2O = C_8H_4O_2 + HBr + CHMeBr\cdot CHO$. The α-bromopropaldehyde was identified by treatment with sodium acetate and then with phenylhydrazine, when Pinkus' acetolphenylhydrazone (Abstr., 1898, i, 224) was obtained. Hydroxyacetone can be prepared from aminoacetone hydrochloride by the action of nitrous acid, and Nef has shown that it is readily formed from α-hydroxypropaldehyde. J. J. S.

Furoylacetic Ester and the Furylpyrazolones. III. Henry A. Torrey and Joaquin E. Zanetti (*Amer. Chem. J.*, 1910, **44**, 5, 391—431. Compare Abstr., 1907, i, 146; 1908, i, 840).—The authors have studied the influence of the furyl group in ethyl furoylacetate and its pyrazolone derivatives, and have synthesised a new analogue of antipyrine containing the furyl group.

An improved method for preparing ethyl furoylacetate is described; the *sodium* and *potassium* salts were prepared; the *oxime*,

$$C_4OH_3\cdot C(NOH)\cdot CH_2\cdot CO_2Et,$$

crystallises in long, white, silky needles, m. p. 131—132°. When hydroxylamine acts on ethyl furoylacetate in the presence of potassium hydroxide, 3-*furyl*isooxazolone, $O<\begin{matrix}N=C\cdot C_4OH_3\\ |\\ CO\cdot CH_2\end{matrix}$, is obtained, crystallising in long, flat needles, m. p. 148—149°.

Ethyl furoylacetate forms a *semicarbazone*, which crystallises in small, flat, rhombic plates, and an *oximino*-derivative,

$$C_4OH_3\cdot CO\cdot C(:NOH)\cdot CO_2Et,$$

m. p. 128—129°. By the action of phenylcarbimide, *ethyl furoylmalonanilate*, $C_4OH_3\cdot CO\cdot CH(CO\cdot NHPh)\cdot CO_2Et$, is produced, crystallising in white needles, m. p. 146—150°.

3-*Furyl*-5-*pyrazolone*, $C_4OH_3\cdot C<\begin{matrix}N{-}{-}NH\\ |\quad\quad|\\ CH_2\cdot CO\end{matrix}$, crystallises in small, rectangular plates, m. p. 223° (decomp.); its *picrate* decomposes at 192°. By the action of acetic anhydride on the pyrazolone, 1-*acetyl*-3-*furyl*-5-*pyrazolone*, m. p. 153—154°, is obtained; the corresponding 1 : 2-*diacetyl* derivative forms long, silky needles, m. p. 102°. *Phenylcarbamyl furylpyrazolone*, $\begin{matrix}C_4OH_3\cdot C{=}{=}N\\ |\quad\quad|\\ CH_2\cdot CO\end{matrix}\!\!>N\cdot CO\cdot NHPh$, m. p. 192°, is obtained by the action of phenylcarbimide on the pyrazolone, and 4-*benzylidene*-3-*furyl*-5-*pyrazolone*, $\begin{matrix}C(C_4OH_3){=}N\\ |\quad\quad|\\ C(:CHPh)\cdot CO\end{matrix}\!\!>NH$, by the

action of benzaldehyde. The azo-derivative, 4-*benzeneazo*-3-*furyl*-5-*pyrazolone*, crystallises in red, transparent prisms, m. p. 182—183°.

1-*Phenyl*-3-*furyl*-5-*pyrazolone hydrochloride*, $C_{13}H_{10}O_2N_2,HCl$, crystallises in small, white needles, m. p. 122—123°. By the action of acetic anhydride on 1-phenyl-3-furyl-5-pyrazolone, 2-*acetyl*-1-*phenyl*-3-*furyl*-5-iso*pyrazolone*, $\begin{matrix}C_4H_3O\cdot C\cdot NAc\\ \|\quad\quad\\ CH\cdot CO\end{matrix}>NPh$, m. p. 69—72°, is obtained in small, flat, slightly yellow prisms. 5-*Benzoyloxy*-1-*phenyl*-3-*furylpyrazole*, $C_4OH_3\cdot C\begin{matrix}N-NPh\\ \|\quad\quad\\ CH:C\cdot OBz\end{matrix}>$, melts at 113—114°, and 4-*oximino*-1-*phenyl*-3-*furyl*-5-*pyrazolone*, $\begin{matrix}C_4OH_3\cdot C=N\\ \|\quad\quad\\ OH\cdot N:C\cdot CO\end{matrix}>NPh$, decomposes at 183—184°. By the action of benzaldehyde on the pyrazolone, 4-*benzylidene*-1-*phenyl*-3-*furyl*-5-*pyrazolone*, decomposing at 210—212°, is obtained. 4-*Benzeneazo*-1-*phenyl*-3-*furyl*-5-*pyrazolone*, $\begin{matrix}C_4OH_3\cdot C=\!=N\\ \|\quad\quad\\ N_2Ph\cdot CH-CO\end{matrix}>NPh$, crystallises in long, light red needles, m. p. 165°. 4-*β*-*Naphthaleneazo*-1-*phenyl*-3-*furyl*-5-*pyrazolone* crystallises in deep, red needles, m. p. 202—203°. The *hydriodide*, m. p. 192—193°; the *hydrochloride*, m. p. 197—198°; the *hydrobromide*, m. p. 194°, and the *picrate*, m. p. 157—158°, of 1-phenyl-3-furyl-2-methyl-5-pyrazolone are described. 4-*Nitroso*-1-*phenyl*-3-*furyl*-2-*methyl*-5-iso*pyrazolone*,

$$\begin{matrix}C_4H_3O\cdot C\cdot NMe\\ \|\quad\quad\\ NO\cdot C-CO\end{matrix}>NPh,$$

crystallises in green needles, m. p. 185°; its *hydrochloride* crystallises in bright red needles, decomposing at 189°.

1-p-*Bromophenyl*-3-*furyl*-5-*pyrazolone*, $\begin{matrix}C_4OH_3\cdot C=\!=N\\ \|\quad\quad\\ CH_2\cdot CO\end{matrix}>N\cdot C_6H_4Br$, prepared from *p*-bromophenylhydrazine and ethyl furoylacetate, crystallises in needles, m. p. 160—161°.

3-*Furyl*-5-*pyrazolone*-1-*benzene*-p-*sulphonic acid* crystallises in small plates, turning brown when kept. 1-m-*Nitrophenyl*-3-*furyl*-5-*pyrazolone* crystallises in yellowish-brown prisms, m. p. 174—175°.

2-*Phenyl*-3-*furyl*-4-iso*pyrazolone*, $\begin{matrix}C_4OH_3\cdot C\cdot NPh\\ \|\quad\quad\\ CH\cdot CO\end{matrix}>NH$, crystallises in transparent prisms, m. p. 176°. N. C.

Quinazolines. XXV. Synthesis of 6- and 7-Amino-2-methyl-4-quinazolones from 4- and 5-Acetylaminoacetylanthranils. Marston T. Bogert, Carl Gustave Amend, and Victor J. Chambers (*J. Amer. Chem. Soc.*, 1910, **32**, 1297—1312).—4- and 5-Acetylaminoacetylanthranils have been prepared by acetylating the corresponding tolylenediamines, oxidising the acetyl derivatives with a neutral solution of potassium permanganate, and treating the resulting diacetylaminobenzoic acids with excess of acetic anhydride. The oxidation of 2 : 5-diacetylaminotoluene proved much more difficult than that of the 2 : 4 compound, and gave a much smaller yield of the diacetylaminobenzoic acid.

When these acetylaminoacetylanthranils are condensed with primary

amines, acetylamino-4-quinazolones are produced, and, on eliminating the acetyl group, the 6- or 7-amino-2-methylquinazolones are obtained. Nearly all the quinazolones now described are crystalline solids of high m. p. or b. p.

4-*Acetylaminoacetylanthranil*, $NHAc\cdot C_6H_3<\begin{matrix}CO\\|\\NAc\end{matrix}$, m. p. 220° (corr.), crystallises in colourless needles. 2 : 5-*Diacetylaminobenzoic acid*, $C_6H_3(NHAc)_2\cdot CO_2H$, m. p. 262° (decomp., corr.), forms minute, colourless crystals. 5-*Acetylaminoacetylanthranil*, m. p. 253° (corr.), crystallises in needles. The 4- and 5-acetylaminoacetylanthranils absorb moisture, and are re-converted into the corresponding diacetylaminobenzoic acids.

The following quinazolones were prepared from 4-acetylaminoacetylanthranil. 7-*Acetylamino*-2-*methyl*-4-*quinazolone* (4-*hydroxy*-7-*acetylamino*-2-*methylquinazoline*),

$$NHAc\cdot C_6H_3<\begin{matrix}N=CMe\\|\\CO-NH\end{matrix} \rightleftarrows NHAc\cdot C_6H_3<\begin{matrix}N=CMe\\|\\C(OH):N\end{matrix},$$

m. p. 344° (corr.), crystallises in slender, silky needles, containing $2H_2O$, and when boiled with dilute potassium hydroxide is converted into 7-amino-2-methyl-4-quinazolone (Bogert and Klaber, Abstr., 1908, i, 466). The latter compound does not react with phenylhydrazine or ethyl chloroacetate; when boiled with formaldehyde and potassium cyanide, a reaction takes place, but the product does not contain any new substances; its *potassium* salt, *hydrochloride*, and *platinichloride* are described.

Dinitro-7-*acetylamino*-2-*methyl*-4-*quinazolone*, m. p. 302° (decomp.), forms orange crystals; the nitro-groups probably occupy the 6- and 8-positions. *Bromo*-7-*acetylamino*-2-*methyl*-4-*quinazolone*, m. p. 292° (corr.), crystallises in minute needles, and, when boiled with 10% potassium hydroxide solution, is converted into *bromo*-7-*amino*-2-*methyl*-4-*quinazolone*, m. p. 272—273° (corr.), which forms light yellow, flaky crystals. 7-*Formylamino*-2-*methyl*-4-*quinazolone*, m. p. 339—340° (corr.), forms colourless, feathery crystals, and the corresponding *propionyl* derivative, m. p. 326—327° (corr.), crystallises in long, white, silky needles. When a solution of 7-amino-2-methyl-4-quinazolone in dilute hydrochloric acid is treated with sodium nitrite at 0° and the product boiled and afterwards neutralised with sodium carbonate, 7-*hydroxy*-2-*methyl*-4-*quinazolone*, $OH\cdot C_6H_3<\begin{matrix}N=CMe\\|\\CO\cdot NH\end{matrix}$, is obtained as a light brown powder, which darkens at about 345°, but does not melt at this temperature; its *acetyl* derivative, m. p. 266° (corr.), forms large, pale brown needles. If the diazotisation product of 7-amino-2-methyl-4-quinazolone is boiled with a solution of copper potassium cyanide, 7-*cyano*-2-*methyl*-4-*quinazolone*, $CN\cdot C_6H_3<\begin{matrix}N=CMe\\|\\CO\cdot NH\end{matrix}$, m. p. 303—304° (corr.), is produced, which crystallises in colourless, feathery needles.

7-*Acetylamino*-2 : 3-*dimethyl*-4-*quinazolone*, $NHAc\cdot C_6H_3<\begin{matrix}N=CMe\\|\\CO\cdot NMe\end{matrix}$,

m. p. 284° (corr.), obtained by the action of methylamine on 4-acetylaminoacetylanthranil, forms colourless, silky needles. *7-Amino-2 : 3-dimethyl-4-quinazolone*, m. p. 224° (corr.), crystallises in needles or prisms; its *platinichloride* is described. *7-Acetylamino-2-methyl-3-ethyl-4-quinazolone*, m. p. 254° (corr.), forms short, colourless needles or lustrous plates. *7-Acetylamino-2-methyl-3-n-propyl-4-quinazolone*, m. p. 206—207° (corr.), crystallises in rosettes of needles. 4-Acetylaminoacetylanthranil does not undergo condensation with *sec.*-butylamine, but yields 2 : 4-*diacetylaminobenzo*-sec.-*butylamide*,

$$C_6H_3(NHAc)_2\cdot CO\cdot NH\cdot C_4H_9,$$

m. p. 235° (corr.), which forms colourless needles. *7-Acetylamino-2-methyl-3-isoamyl-4-quinazolone* has m. p. 288° (corr.), and the corresponding *3-phenyl*, 3-p-*anisyl*, 3-p-*phenetyl*, and 3-*α-naphthyl* derivatives have m. p. 276°, 273°, 259°, and 256° (corr.) respectively. When 4-acetylaminoacetylanthranil is heated with *p*-aminobenzonitrile, a quinazolone is not produced, but a *compound*, m. p. 258° (corr.), is obtained, containing 12·4% of nitrogen.

When hydrazine hydrate (1 mol.) is boiled with 4-acetylaminoacetylanthranil (1 mol.), *3-amino-7-acetylamino-2-methyl-4-quinazolone*, m. p. 268° (corr.), is produced, which crystallises with $1H_2O$, and fails to give the Bülow condensation (Abstr., 1906, i, 906, 981) with ethyl diacetylsuccinate; the *hydrochloride* has m. p. 312° (decomp.). If 4-acetylaminoacetylanthranil is treated in the cold with 50% hydrazine hydrate solution, 2 : 4-*diacetylaminobenzoylhydrazide*,

$$C_6H_3(NHAc)_2\cdot CO\cdot NH\cdot NH_2,$$

is produced, which crystallises in short, slender needles, and melts at 268° with formation of 7-acetylamino-3-amino-2-methyl-4-quinazolone. 3 : *7-Diacetylamino-2-methyl-4-quinazolone*, m. p. 304° (corr.), forms minute, colourless crystals, and, when boiled with dilute potassium hydroxide, is converted into 3 : *7-diamino-2-methyl-4-quinazolone*, m. p. 238° (corr.), which forms silky needles.

3-Anilino-7-acetylamino-2-methyl-4-quinazolone,

$$NHAc\cdot C_6H_3\langle \begin{matrix} N{=}CMe \\ CO\cdot N(NHPh) \end{matrix}$$

m. p. 214° (corr.), obtained by the action of phenylhydrazine on 4-acetylaminoacetylanthranil, forms colourless, feathery needles.

7-Acetylamino-2-methyl-4-quinazolonyl-3 : 7′-(2′-methyl-4′-quinazolone),

$$NHAc\cdot C_6H_3\langle \begin{matrix} N{=}CMe \\ CO{-}N\cdot C_6H_3\langle \begin{matrix} N{=}CMe \\ CO\cdot NH \end{matrix} \end{matrix}$$

m. p. 335° (corr.), obtained by the condensation of 7-amino-2-methyl-4-quinazolone with 4-acetylaminoacetylanthranil, crystallises in short, stout, pale yellow needles.

The following quinazolones were prepared from 5-acetylaminoacetylanthranil. *6-Acetylamino-2-methyl-4-quinazolone*, m. p. 350° (corr.), forms colourless needles or prisms. *6-Amino-2-methyl-4-quinazolone*, m. p. 314—315° (corr.), crystallises in rosettes of needles. *6-Acetylamino-2 : 3-dimethyl-4-quinazolone*, m. p. 278° (corr.), and *6-acetylamino-2-methyl-3-ethyl-4-quinazolone*, m. p. 229° (corr.), form colourless, silky needles. The corresponding 3-n-*propyl* and *3-phenyl*

derivatives have m. p. 181° and 255° (corr.) respectively. 3-*Amino*-6-*acetylamino*-2-*methyl*-4-*quinazolone*, m. p. 262—263° (corr.), obtained by heating 5-acetylaminoacetylanthranil with dilute hydrazine hydrate, crystallises in rosettes of colourless, silky needles. E. G.

Diguanide and Compounds Derived from It. Karol Rackmann (*Annalen*, 1910, 376, 163—183. Compare Bamberger and Dieckmann, Abstr., 1892, 737; Söll and Stutzer, this vol., i, 14).—Diguanide has been prepared by a modification of Herth's method (Abstr., 1881, 896), using soda-water bottles in place of sealed tubes. The sulphate can be obtained from the copper derivative by treatment with 10% sulphuric acid, and the free base from the sulphate by the action of barium hydroxide. Diguanide, $NH[C(NH_2):NH]_2$, crystallises from absolute alcohol in glistening prisms, m. p. 130°, and its aqueous solution decomposes gradually when kept. The *carbonate*, $C_2H_5N_7,H_2CO_3$, crystallises in prisms, sparingly soluble in alcohol; the normal *hydrochloride*, $C_2H_5N_7,HCl$, forms glistening needles, m. p. 235°, and the acid *hydrochloride*, $C_2H_5N_7,2HCl$, large plates, m. p. 248°. The *nitrate*, $C_2H_5N_7,HNO_3$, crystallises in large, glistening prisms, m. p. 192°; the *acetate*, $C_2H_5N_7,CH_3\cdot CO_2H$, has m. p. 268°, the *oxalate*, $C_2H_5N_7,C_2O_4H_2$, m. p. 210°, and the *chloroacetate*, m. p. 186°. The *cyanoacetate* forms soluble, glistening plates, and the *succinate*, $2C_2H_5N_7,C_2H_4(CO_2H)_2$, colourless crystals.

Oxalyldiguanide, $\begin{matrix}CO\cdot NH\cdot C(:NH)\\ |\\ CO\cdot NH\cdot C(:NH)\end{matrix}\!\!>\!NH$, prepared by the action of ethyl oxalate on diguanide, crystallises from alcohol in large, colourless needles, which decompose above 300°. It does not react with ethyl oxalate or ethyl malonate, but when warmed with dilute hydrochloric acid yields *diguanidino-oxalic acid*,

$$CO_2H\cdot CO\cdot NH\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NH_2,$$

which crystallises in long, thin needles, m. p. 240°. The *sodium* salt, $C_4H_6O_3N_5Na$, forms long needles, and the *barium* salt, small, sparingly soluble needles.

Malonyldiguanide (4 : 6-*diketo*-2-*guanidinopyrimidine*),

$$NH:C(NH_2)\cdot NH\cdot C\!<\!\begin{matrix}NH\cdot CO\\ |\\ N-CO\end{matrix}\!\!>\!CH_2,$$

prepared by boiling an alcoholic solution of diguanide with ethyl malonate, crystallises in small needles, and has not acidic properties. The *hydrochloride*, $C_5H_7O_2N_5,HCl$, forms feathery needles, and the *sulphate*, $2C_5H_7O_2N_5,H_2SO_4$, large needles. *Succinyldiguanide*,

$$NH:C(NH_2)\cdot NH\cdot C\!<\!\begin{matrix}NH\cdot CO\cdot CH_2\\ |\\ N-CO-CH_2\end{matrix},$$

is only formed in the absence of all traces of water, and has feebly basic properties. The *sulphate*, $C_6H_9O_2N_5,H_2SO_4$, crystallises in large needles, the *hydrochloride*, $C_6H_9O_2N_5,2HCl$, in slender needles, and the *picrate*, $C_6H_9O_2N_5,C_6H_3O_7N_3$, in brilliant, large needles, m. p. 220°.

A theoretical yield of ammeline can be obtained by condensing diguanide with an absolute alcoholic solution of ethyl carbonate, and a theoretical yield of thioammeline by condensing diguanide with an alcoholic solution of hydrogen sulphide. The symmetrical constitu-

tional formulæ for these two compounds are regarded as established beyond dispute by those syntheses, and also the symmetrical formulæ of other cyanuric acid derivatives.

When diguanide is condensed in aqueous solution with carbon disulphide, the *product* consists of somewhat unstable, reddish-brown crystals, $C_3H_5N_5S_2$.

Formylguanamine (1 : 3-diamino-1 : 3 : 5-triazine) (Bamberger and Dieckmann : Abstr., 1892, *loc. cit.*) can be synthesised from diguanide and ethyl formate in absolute alcoholic solution.

Phenylguanamine (3 : 5-*diamino*-1-*phenyl*-1 : 3 : 5-*triazine*),

$$N\lessdot\begin{matrix}C(NH_2)\cdot N\\ C(NH_2):N\end{matrix}\gtrdot CPh,$$

prepared by the action of benzoyl chloride and alkali on diguanide sulphate, crystallises from water in large prisms, m. p. 222°, and yields a *picrate*, m. p. 228°.

Diguanide reacts with an alcoholic solution of chloroacetic acid, yielding *diguanidinoacetic acid*, $C_2H_6N_5\cdot CH_2\cdot CO_2H$, in the form of its hydrochloride. The acid crystallises from aqueous alcohol in long needles, and reacts with both acids and alkalis. The *sodium* salt, $C_4H_8O_2N_5Na$; *hydrochloride*, $C_4H_9O_2N_5,HCl$, and *picrate*,

$$C_4H_9O_2N_5,C_6H_3O_7N_3,$$

m. p. 202°, are described. J. J. S

Synthesis of Tetrazoles from Arylazoimides. Otto Dimroth and Siegfried Merzbacher (*Ber.*, 1910, **43**, 2899—2904. Compare Abstr., 1907, i, 659).—Extending to acetaldehydephenylhydrazone and glyoxylic acid phenylhydrazone the reaction with phenylazoimide previously studied, the authors have been able to isolate *N*-benzeneazoacetophenylhydrazidine, NHPh·N:N·CMe:N·NHPh or

NPh:N·NH·CMe:N·NHPh,

and *N*-benzeneazo-oxalophenylhydrazidine,

NHPh·N:N·C(CO$_2$H):N·NHPh,

as intermediate products. The former substance when treated with hydrochloric acid yields benzenediazonium chloride and acetophenylhydrazidine, $CMe(NH_2):N\cdot NHPh$. The second product cannot be decomposed in that way, but benzeneazo-5-hydroxy-1-phenyl-1 : 2 : 3-triazole (compare Dimroth and Eberhardt, Abstr., 1905, i, 99) is formed when its sodium salt is treated with benzoyl chloride and sodium hydroxide. These hydrazidine derivatives could not be converted into tetrazoles. When, however, tribromophenylazoimide reacts with the hydrazones mentioned, the intermediate products are labile; they lose tribromoaniline spontaneously, 1-phenyl-4-methyl-1 : 2 : 3 : 5-tetrazole and 1-phenyl-1 : 2 : 3 : 5-tetrazole-4 carboxylic acid being obtained.

N-*Benzeneazoacetophenylhydrazidine*, obtained by heating acetaldehydephenylhydrazone and phenylazoimide in alcoholic sodium ethoxide solution for forty hours on the water-bath, crystallises in reddish-yellow, rhomboidal tablets, m. p. 101° (with evolution of gas). In contact with dilute hydrochloric acid, it gradually dissolves with evolution of gas, and from the solution *acetophenylhydrazidine hydrochloride*, $C_8H_{12}N_3Cl,\frac{1}{2}H_2O$, can be obtained (compare

Voswinckel, Abstr., 1902, i, 844). It melts at 140°, resolidifies, and melts again (not sharply) at 205°.

The *sodium* salt of N-*benzeneazo-oxalomonophenylhydrazidine*, $C_{14}H_{12}O_2N_5Na,3H_2O$, is prepared by heating glyoxylic acid phenylhydrazone and phenylazoimide in alcoholic sodium ethoxide solution for fifteen minutes on the water-bath. It is a yellow, crystalline substance, which becomes red in excess of sodium hydroxide in consequence of the formation of a disodium salt. With acids, it yields the free *acid* as a flocculent precipitant, which soon decomposes with evolution of gas even in the cold.

1-*Phenyl*-4-*methyl*-1 : 2 : 3 : 5-*tetrazole*, $PhN{<}\overset{|\_\_\_\_\_|}{N{\cdot}N{:}N{\cdot}CMe{:}N}$, is best freed from the accompanying tribromoaniline by extraction with ether and subsequent distillation in a vacuum, the distillate being collected at 140°/15 mm. It crystallises in long, flat, colourless needles, m. p. 40°, and has an odour of jasmine, although the isomeric 1-phenyl-5-methyl-1 : 2 : 3 : 4-tetrazole (following abstract) has no smell.

R. V. S.

Diazohydrazides. Otto Dimroth and Guillaume de Montmollin (*Ber.*, 1910, **43**, 2904—2915. Compare preceding abstract).—The diazohydrazides from monoacylhydrazines condense to 1 : 2 : 3 : 4-tetrazoles when treated with alkalis, indicating that they are *β*-diazohydrazides of the type $NAr{:}N{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}R$ (compare Curtius, Abstr., 1893, i, 463). The diazo-derivatives of the diacylhydrazines also yield tetrazoles with alkalis, an acyl group being eliminated, and in many cases (for example, 5-hydroxy-1-phenyltetrazole) this synthesis offers the best means of preparing tetrazole derivatives. It was not found possible to prepare the bisdiazohydrazides, $NAr{:}N{\cdot}NAc{\cdot}NAc{\cdot}N{:}NAr$, from which pentazoles might have been obtained by a method analogous to that described in the preceding abstract. Only monoacyldiazohydrazides can react with a second molecule of a diazonium salt, and they then undergo a tautomeric rearrangement, such that the reaction product spontaneously decomposes into the diazoamido-compound and the azoimide of the acid group.

Diacylhydrazines do not react with diazonium salts in acid solution. The diazohydrazides are readily obtained as white or yellow, usually flocculent, precipitates, however, when aqueous solutions of the diacylhydrazides are treated with a slight excess of sodium carbonate, and then with the equivalent quantity of the neutralised diazonium chloride solution. The temperature is maintained at $-10°$, salt being added to prevent freezing. On addition of sodium hydroxide, the precipitate is converted into the tetrazole derivative. 1-Phenyl-1 : 2 : 3 : 4-tetrazole was obtained by the use of diformylhydrazine (the diazohydrazide from which is very unstable), and it has the properties formerly described. 1-p-*Tolyl*-1 : 2 : 3 : 4-*tetrazole*, $C_8H_8N_4$, forms colourless needles, m. p. 96°. 1-*p*-Nitrophenyltetrazole may be obtained similarly.

1-*Phenyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazole*, $NPh{<}\overset{|\_\_\_\_\_|}{N{\cdot}N{:}N{\cdot}N{:}CMe}$ (from

diacetylhydrazine), forms lanceolate crystals, m. p. 97·5°. p-*Toluene-azodiacetylhydrazine*, $C_7H_7N_2{\cdot}NAc{\cdot}NHAc$, is more stable than the phenyl derivative. It forms small, pale brown crystals, m. p. 60° (decomp.). 1-p-*Tolyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazole*, $C_9H_{10}N_4$, has m. p. 106°. p-*Nitrobenzeneazodiacetylhydrazine*, $C_{10}H_{11}O_4N_5$, forms colourless, lustrous crystals, m. p. 107° (with evolution of gas). It can be preserved unchanged in the dry state for months. 1-p-*Nitrophenyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazole*, $C_8H_7O_2N_5$, crystallises in pale yellow plates, m. p. 129°.

The diazohydrazides from dibenzoylhydrazine are more unstable than those from diacetylhydrazine. It is necessary to dissolve the hydrazine in dilute sodium hydroxide, owing to its slight solubility in water. *Benzeneazodibenzoylhydrazine* was obtained as a white, unstable precipitate.

5-Hydroxy-1-phenyl-1 : 2 : 3 : 4-tetrazole, obtained from ethyl hydrazinedicarboxylate and benzenediazonium chloride, is identical with the phenylhydroxytetrazole of Freund and Hempel (Abstr., 1895, i, 193).

Tribromobenzenediazonium salts react (but incompletely) with ethyl hydrazinedicarboxylate in weakly acid solution. *Ethyl tribromo-benzeneazohydrazinedicarboxylate*, $C_6H_2Br_3N_2{\cdot}N(CO_2Et){\cdot}NH{\cdot}CO_2Et$, is better obtained in presence of sodium carbonate. It forms small, colourless needles, which explode at 111—115°, according to the rate of heating. The compound can be preserved unchanged. Ethereal hydrogen chloride decomposes it into its components. It was not possible to prepare the corresponding tetrazole.

The monoacylhydrazines react with diazonium salts, not only in alkaline, but also in acid solution. Most of the diazohydrazides are too unstable to be isolated and purified. *Benzeneazoacethydrazide* and p-*tolueneazoacethydrazide* are white precipitates, which are rapidly converted into the tetrazoles when treated with sodium hydroxide. p-*Nitrobenzeneazoacethydrazide*, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}NH{\cdot}NHAc$, is soluble in dilute sodium hydroxide with production of an intense, bluish-red coloration, which afterwards disappears, and the tetrazole is formed. With *p*-toluenediazonium chloride in solution containing alkali hydroxide, it yields *p*-nitrobenzenediazoaminotoluene (Bamberger, Abstr., 1895, i, 351), a smell of *p*-tolylazoimide is observed, and azoimide is found in the filtrate. *Sulphobenzeneazoacethydr-azide*, $SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}NH{\cdot}NH{\cdot}Ac$, is obtained by the method described in the form of its *sodium* salt, which is very stable when dry. Water slowly effects an anomalous decomposition, azoimide and sodium sulphanilate being produced. The substance reacts with *p*-toluenediazonium chloride only in the presence of sodium hydroxide, azoimide and sodium *p*-toluenediazoaminobenzenesulphonate being formed. With sodium hydroxide the diazohydrazide yields the *sodium* salt of 1-*phenyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazolesulphonic acid*,

$$SO_3H{\cdot}C_6H_4{\cdot}N{\cdot}N{:}N{\cdot}N{:}CMe,$$

in crystalline form. The *silver* salt, $C_8H_7O_3N_4SAg$, crystallises in flat, lustrous prisms.

Benzeneazobenzhydrazide (Curtius, *loc. cit.*) is converted by sodium

hydroxide into 1 : 5-diphenyl-1 : 2 : 3 : 4-tetrazole, identical with that of Schröter (Abstr., 1909, i, 617, 773).

5-Phenyl-1-p-nitrophenyl-1 : 2 : 3 : 4-tetrazole, $C_{13}H_9O_2N_5$, is produced, in addition to *p*-nitrophenylazoimide and a green *sodium* salt, when *p*-nitrobenzeneazobenzhydrazide (von Pechmann, Abstr., 1896, i, 678) is dissolved in sodium hydroxide. It forms yellow prisms, m. p. 149°. The nitrophenylphenyltetrazole, m. p. 177—178°, obtained by Schröter must therefore have the structure:

$$Ph\cdot\underset{|}{N}\cdot N:N\cdot N:\underset{|}{C}\cdot C_6H_4\cdot NO_2.$$

Semicarbazide reacts with benzene- and with *p*-toluene-diazonium chlorides in acetic acid solution, yielding crystalline diazohydrazides. The *toluene* derivative is the more stable. It forms colourless laminæ, which decompose rapidly even when dry. An ethereal solution, when kept in the cold, deposits carbamoazoimide of m. p. 97°, and in the filtrate *p*-toluidine is present. Tolueneazosemicarbazide does not yield the corresponding tetrazole when treated with alkali. The action of a cold alcoholic solution of sodium ethoxide gives rise to sodium azoimide, diazoaminotoluene, *p*-toluidine, and sodium carbonate. Hence it is possible that in this diazohydrazide the azo-group is attached in the α-position. R. V. S.

Action of Diazo-compounds on Ethyl Glutaconate. Ferdinand Henrich, W. Reichenburg, G. Nachtigall, W. Thomas, and C. Baum (*Annalen*, 1910, **376**, 121—151. Compare Abstr., 1899, i, 794; Dimroth and Hartmann, Abstr., 1909, i, 66).—The products obtained by the action of diazonium salts (1 mol.) on ethyl glutaconate are yellow, and have the constitution of azo-compounds, for example,

$$CO_2Et\cdot CH:CH\cdot CH(CO_2Et)\cdot N:NPh,$$

or the tautomeric hydrazone formula,

$$CO_2Et\cdot CH:CH\cdot C(CO_2Et):N\cdot NHPh.$$

The fact that they can be boiled with alcohol or even distilled without decomposition and that they do not couple with R-salt indicates that they cannot have the diazo-constitution $>C(OEt)\cdot O\cdot N_2R$ (compare Dimroth, *loc. cit.*), although it is highly probable that such diazo-compounds are formed as unstable intermediate products in the preparation of the stable azo-compounds.

The condensation takes place most readily in an aqueous alcoholic solution of the ester, and in the presence of sodium acetate and an aqueous solution of the diazonium salt. The reaction proceeds slowly, and is complete in half to one hour.

When an excess of diazonium salt is used, a compound of the type $CO_2Et\cdot C(N_2Ph):CH\cdot C(CO_2Et):N\cdot NHPh$ is formed. These compounds are quite different from the formazyl derivatives described previously, (Heinrich and Thomas, Abstr., 1908, i, 114); they have an intense red colour, and readily lose the elements of ethyl alcohol when heated with alcohol, yielding pyridazone derivatives:

$$CO_2Et\cdot C(:N\cdot NHR)\cdot CH:C(CO_2Et)\cdot N:NR \longrightarrow$$

$$EtOH + CH<\begin{matrix}C(CO_2Et)=N\\C(N:NPh)\cdot CO\end{matrix}>NR$$

This decomposition proceeds at very different rates with the different condensation products, those containing ortho-substituents in the benzene nuclei being most stable. When such substituents are present, the elimination of the alcohol is effected by heating with acetic anhydride, but in the case of the mesitylene derivative, even this reagent is without action. The stability of the compounds depends not merely on the positions of the substituents, but also on their chemical nature, the more electro-positive the ortho-substituent the greater its stabilising effect. The pyridazone derivatives are brown or brownish-yellow solids, the colour being palest when halogen substituents are present in *m*- or *p*-positions; they are stable towards dilute acids or aqueous solutions of alkalis, but dissolve in concentrated sulphuric acid, yielding reddish-yellow solutions.

Ethyl glutacononate phenylhydrazone,

$$CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NHPh$$

(or desmotropic formula), separates from alcohol in long, pale yellow, glistening crystals, m. p. 67—68°. *Ethyl 3-benzeneazoglutacononate phenylhydrazone*, $N_2Ph\cdot C(CO_2Et){:}CH\cdot C(CO_2Et){:}N\cdot NHPh$, separates from a boiling mixture of benzene and light petroleum (1 : 4) in brilliant, glistening, rhombic crystals [$a:b:c = 0{\cdot}4423:1:0{\cdot}6561$], m. p. 117° (decomp); it gives Bulow's reaction, and is decomposed to a certain extent when boiled for some time with benzene. *Ethyl 5-benzeneazo-1-phenyl-6-pyridazone-3-carboxylate*,

$$CH\begin{matrix}<(CO_2Et)=N\\(N_2Ph)-CO>\end{matrix}NPh,$$

crystallises from alcohol in brownish-yellow needles, m. p. 161°.

Ethyl 3-o-*tolueneazoglutacononate* o-*tolylhydrazone*,

$$C_6H_4Me\cdot N{:}N\cdot C(CO_2Et){:}CH\cdot C(CO_2Et){:}N\cdot NH\cdot C_6H_4Me,$$

forms dark red, glistening crystals, m. p. 134°, after sintering at 130°, and the corresponding *ethyl* 5-o-*tolueneazo*-1-o-*tolyl*-6-*pyridazone*-3-*carboxylate*, $C_{21}H_{20}O_3N_4$, crystallises in dark brown needles, m. p. 152° after sintering at 150°; the isomeric 5-p-*tolueneazo*-1-p-*tolyl* compound forms pale brown-coloured needles, m. p. 157°, and is prepared readily from *ethyl* 3-p-*tolueneazoglutacononate* p-*tolylhydrazone*, $C_{23}H_{26}O_4N_4$, which resembles the ortho-compound, and has m. p. 124—125° after sintering at 120°.

Ethyl glutacononate as.-m-*xylylhydrazone*,

$$CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NH\cdot C_6H_3Me_2,$$

crystallises from dilute alcohol in pale yellow, glistening needles, m. p. 107°, and *ethyl* m-*xyleneazoglutacononate* m-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N{:}N\cdot C(CO_2Et){:}CH\cdot C(CO_2Et){:}N\cdot NH\cdot C_6H_3Me_2,$$

in bright red, glistening prisms, m. p. 160—161°.

Ethyl 5-m-*xyleneazo*-1-m-*xylyl*-6-*pyridazone*-3-*carboxylate*,

$$C_{23}H_{24}O_3N_4,$$

crystallises from alcohol in brilliant, brown prisms, m. p. 155° after sintering at 150°. *Ethyl glutacononate mesitylhydrazone*,

$$CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NH\cdot C_6H_2Me_3,$$

separates from dilute alcohol in yellow, glistening crystals, m. p. 79—80°. *Ethyl* 3-*mesityleneazoglutacononate mesitylhydrazone*,

$$C_{27}H_{34}O_4N_4,$$

separates from light petroleum in glistening, red crystals, m. p. 143—150°, and does not yield a pyridazone derivative. *Ethyl glutacononate* o-*phenetylhydrazone*,

$$CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NH\cdot C_6H_4\cdot OEt,$$

forms glistening, yellow crystals, m. p. 85°, and *ethyl* o-*phenetoleazoglutacononate* o-*phenetylhydrazone*,

$$OEt\cdot C_6H_4\cdot N{:}N\cdot C(CO_2Et){:}CH\cdot C(CO_2Et){:}N\cdot NH\cdot C_6H_4\cdot OEt,$$

crystallises from benzene in dark red, glistening prisms, m. p. 195°.

Ethyl p-*chlorobenzeneazoglutacononate* p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot N{:}N\cdot C(CO_2Et){:}CH\cdot C(CO_2Et)\cdot N{:}NH\cdot C_6H_4Cl,$$

crystallises in orange-coloured prisms, m. p. 138°, and when heated with alcohol yields *ethyl* 5-p-*chlorobenzeneazo*-1-p-*chlorophenyl*-6-*pyridazone*-3-*carboxylate*, $C_{19}H_{14}O_3N_4Cl_2$, as pale brown needles, m. p. 208—209° after sintering at 205°. *Ethyl* 3-m-*bromobenzeneazoglutacononate* m-*bromophenylhydrazone*, $C_{21}H_{20}O_4N_4Br_2$, also forms orange-coloured crystals, and has m. p. 130°; *ethyl* 5-m-*bromobenzeneazo*-1-m-*bromophenyl*-6-*pyridazone*-3-*carboxylate*, $C_{19}H_{14}O_3N_4Br_2$, forms pale brown, microscopic needles, m. p. 149°. The isomeric *o*-bromo-derivatives of the glutacononate and pyridazone compounds melt respectively at 143—144° and 166—167°, and the *p*-bromo-derivatives at 140° and 229°.

Ethyl glutacononate p-*nitrophenylhydrazone*,

$$CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

forms a yellow, crystalline powder, m. p. 109°.

Formazyl-α-methylacrylic acid, $NHPh\cdot N{:}C(N{:}NPh)\cdot CH{:}CMe\cdot CO_2H$, is formed by the action of benzenediazonium chloride (2 mols.) on methylglutaconic acid in dilute acetic acid solution (compare Abstr., 1908, i, 114), and crystallises from alcohol in dark-coloured needles, m. p. 193° (decomp.). It yields a sparingly soluble, reddish-brown, silver salt. J. J. S.

Decomposition of Azopyrazolones by means of Concentrated Nitric Acid. Carl Bülow, Karl Haas, and, in part, with Hermann Schmachtenberg (*Ber.*, 1910, **43**, 2647—2662).—Rothenburg's 4-benzeneazo-3-methyl-5-pyrazolone (Abstr., 1895, i, 687) can be prepared by the condensation of hydrazine hydrate with ethyl phenylazoacetoacetate in acetic acid solution. Nitric acid reacts with this pyrazolone, yielding first an additive compound, $C_{10}H_{10}ON_4,2HNO_3$, and finally an orange-yellow nitro-derivative, which has been shown to be 4-*p*-nitrobenzeneazo-3-methyl-5-pyrazolone, as it can be synthesised from ethyl *p*-nitrophenylazoacetoacetate and hydrazine hydrate. Further reaction with nitric acid decomposes the nitroazopyrazolone derivative into Betti's 4-nitro-3-methyl-5-pyrazolone (Abstr., 1904, i, 533) and benzenediazonium nitrate. This decomposition, which proceeds according to the equation: $C_{10}H_{10}ON_4 + 2HNO_3 = H_2O + N_2PhNO_3 + C_4H_5O_3N_3$, is used in favour of the azo-structure of the original compound, since Schmidt (Abstr., 1905, i, 951) has shown that true azo-dyes react with concentrated nitric acid, yielding the diazo-compound used in the preparation of the dye, and a nitro-derivative of the compound, which was "coupled" with the diazo-solution. Knorr's

suggestion that the azo-derivatives of pyrazolone are hydrazones is thus incorrect.

Similarly, the products obtained by the action of diazonium salts on 3-substituted *iso*oxazolones (Claisen and Zedel, Abstr., 1891, 468) are azo-derivatives (*o*-hydroxyazo-compounds), as they are decomposed by nitric acid in acetic acid solution, yielding a diazonium nitrate and a nitro-derivative of the *iso*oxazolone, for example:

$$\begin{matrix}O\cdot C(OH)\\ \vert \\ N{=}{=}CR\end{matrix}\!\!>C\cdot N{:}NR + 2HNO_3 = RN_2\cdot NO_3 + H_2O + \begin{matrix}O\cdot C(OH)\\ \vert \\ N{-}{-}CR\end{matrix}\!\!>C\cdot NO_2.$$

Knorr's 4-nitro-1-phenyl-3-methyl-5-pyrazolone (Abstr., 1887, 601) and Betti's 4-nitro-3-methyl-5-pyrazolone are represented by hydroxylic and not ketonic formula; for example, the latter as

$$\begin{matrix}NH\cdot C(OH)\\ \vert \\ N{=}{=}CMe\end{matrix}\!\!>C\cdot NO_2,$$

since the hydroxylic structure accounts for the pronounced acidic character of these nitro-compounds; for example, their alkali salts are neutral.

The primary product of the condensation of ethyl phenylazoacetoacetate and hydrazine hydrate in cold glacial acetic acid crystallises in glistening, red needles, m. p. 167°; when boiled with alcohol or glacial acetic acid it yields 4-benzeneazo-3-methyl-5-pyrazolone; when boiled with an acetic acid solution of phenylhydrazine it yields 4-benzeneazo-1-phenyl-3-methylpyrazolone, and when heated for a few minutes with an 80% acetic acid solution of benzhydrazide it yields ethyl phenylazoacetoacetate benzoylhydrazone, m. p. 146°. All these reactions indicate that the red compound is to be represented as $N_2H_2[CMe{:}C(N_2Ph)\cdot CO_2Et]_2$.

4-Nitro-5-hydroxy-3-methylpyrazole (4-nitro-3-methyl-5-pyrazolone) crystallises from acetic acid in prisms, m. p. 267° (decomp.), but cannot be acetylated. Its alkali salts are neutral, and hence the hydroxy-compound can be titrated by means of a standard alkali hydroxide solution, using phenolphthalein as indicator. The following salts are described: *potassium*, $C_4H_4O_3N_3K$; *ammonium*, yellow needles, decomposing at 248°; *hydrazine*, $C_4H_5O_3N_3,N_2H_4,H_2O$, glistening, yellow needles; *barium*, long, golden-yellow, compact prisms; *zinc*, yellow needles; *aluminium*, slender, yellow needles; *silver*, yellow plates, and also *copper*, *lead*, *cobalt*, and *nickel* salts.

4-Benzeneazo-5-hydroxy-3-methylpyrazole reacts with aqueous nitrous acid, yielding *4-benzeneazo-1-nitroso-5-hydroxy-3-methylpyrazole*, $NPh{:}N\cdot C\!\!<\!\!\begin{matrix}C(OH)\cdot N\cdot NO\\ CMe{=}N\end{matrix}$, which crystallises in slender needles, decomposing at 135°. The nitroso-group can be eliminated by warming for a short time with dilute sodium hydroxide solution, or with 15% hydrochloric acid, yielding the original hydroxypyrazole. The nitroso-compound is also decomposed when boiled with alcohol, acetone, or glacial acetic acid, and reacts with an excess of nitrous acid, yielding as final product 2 : 4-dinitrophenol.

When reduced with stannous chloride and hydrochloric acid 4-benzeneazo-5-hydroxy-3-methylpyrazole yields aniline and *4-amino 5-hydroxy-3-methylpyrazole*, but the latter cannot be isolated on

account of the readiness with which it undergoes oxidation into a homologue of rubazonic acid, m. p. 238°.

The same acid is formed, together with a stable product, $C_4H_6O_2N_2$, by the action of oxidising agents on the reduction product of 4-nitro-5-hydroxy-3-methylpyrazole.

4-*m*-Xyleneazo-5-hydroxy-3-methylpyrazole also reacts with nitric acid, yielding 4-nitro-3-methylpyrazolone and *m*-xylenediazonium nitrate.

Nitric acid reacts with ethyl phenylazoacetoacetate, yielding ethyl *p*-nitrophenylazoacetoacetate. J. J. S.

Monosubstituted Triazens and Attempts to Prepare Triazen. Otto Dimroth and Karl Pfister (*Ber.*, 1910, **43**, 2757—2767).—By the reduction of phenylazoimide by stannous chloride in ethereal solution, phenyltriazen is obtained (Dimroth, Abstr., 1907, i, 653). The reaction has been extended to substituted azides, some few of which are more stable than phenyltriazen, but the majority are less stable, decomposing on formation into amine and nitrogen. Benzylazoimide is much less easily reduced than phenylazoimide, and the triazen decomposes immediately on formation.

Attempts to reduce azoimide to triazen by a variety of methods were without success, but it is believed that triazen can exist for a short time in aqueous solution at $-10°$.

The reductions were carried out at $-15°$ to $-18°$ in dry ether, moisture being carefully excluded; the stannochloride of the triazen crystallises from the mixture, and can be kept without decomposition for some hours in a freezing mixture.

p-*Tolylazoimide* is an oil of characteristic anis-like odour, b. p. 80°/10 mm. o-*Bromophenylazoimide* is obtained pure on distillation in steam; o-*bromophenyltriazen* is extremely unstable; m-*bromophenylazoimide* has b. p. 99°/100 mm.; m-*bromophenyltriazen* is extremely unstable, and explodes on gentle heating.

p-*Bromophenyltriazen* is more stable; the *cuprous* compound,

$$C_6H_5BrN_3Cu,$$

forms yellow crystals, and explodes in the flame. The free triazen separates in long, colourless platelets when freshly prepared, m. p. 36·5°, decomposing into nitrogen and bromoaniline; older samples undergo a change manifested by a visible movement in the crystals, and have m. p. 39°. Solution in ether and precipitation with light petroleum gives the more fusible modification. Generally, *p*-bromophenyltriazen is more stable than phenyltriazen; when brought together with benzaldehyde in ethereal solution at $-15°$, it decomposes.

2 : 4 : 6-Tribromophenyltriazen could not be obtained from tribromophenylazoimide.

Similarly, *p*-methoxyphenylazoimide, which forms crystals, m. p. 36°, does not give a triazen on reduction.

Ethyl p-*azoimidobenzoate* is volatile in steam, and has b. p. 150°/10 mm., m. p. 18°. *Ethyl* p-*triazenobenzoic acid*, $C_6H_4(CO_2Et)\cdot N_3H_2$, forms a relatively stable stannochloride. The *cuprous* salt forms lustrous, golden platelets, decomp. 130°, and can be kept for some months. The free triazen crystallises in lustrous granules or feathery needles, m. p. 68° (decomp.). It conbines with phenyl cyanate to an *azocarbamide*,

$CO_2Et\cdot C_6H_4\cdot N{:}N\cdot NH\cdot CO\cdot NHPh$, which crystallises in colourless, lustrous, thin, six-sided plates, m. p. 135° (decomp.). It dissolves in dilute sodium hydroxide with an intense yellow coloration, forming on the addition of acetic acid the *carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot N{:}N\cdot NH\cdot CO\cdot NHPh,$$

crystallising in colourless needles, m. p. 172°.

With formaldehyde, the triazen condenses to form a *compound*,

$$CO_2Et\cdot C_6H_4\cdot N_2\cdot NH\cdot CH_2\cdot NH\cdot N_2\cdot C_6H_4\cdot CO_2Et,$$

decomp. at 48° to ethyl methylenedi-*p*-aminobenzoate, m. p. 188°.

p-Benzoylphenylazoimide crystallises in pale yellow, lustrous plates, m. p. 74·5°. The corresponding triazen is relatively stable; it dissolves in ether without the formation of gas, and can be kept in a desiccator for a day.

α- and β-Naphthylazoimides did not yield triazens on reduction.

E. F. A.

Ionisation, Hydration, and Optical Rotation of White of Egg. Wolfgang Pauli (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 241—243).—The author gives a brief summary of observations which indicate that egg-albumin behaves as a weak amphoteric electrolyte. The properties of acid and alkaline solutions seem to show that the positive and negative albumin ions are combined with a very large number of molecules of water. The hydration which accompanies ionisation gives rise to considerable differences in the optical rotatory power and the viscosity of egg-albumin solutions. The readiness with which albumin ions are formed by different acids is not simply determined by the relative strengths of the acids, although this appears to be the case for the formation of negative ions on addition of different mono-acid bases.

The phenomenon of ionic hydration, which is so strongly developed in the case of albumin, is supposed to be analogous to that of gelatinisation. H. M. D.

General Protein Chemistry. II. Precipitation of Globulins at the Isoelectric Point. Peter Rona and Leonor Michaelis (*Biochem. Zeitsch.*, 1910, 28, 193—199. Compare this vol., i, 646).—It was shown in a previous paper that the sedimentation rate of denatured albumin attains a maximum when the hydrogen ion concentration is that of the isoelectric point, and the same is now shown to be the case for solutions of ordinary (not denatured) serum-globulin, edestin, gliadin, and casein. On this behaviour is based a clear distinction between globulins and albumins; the former are "denaturable" proteins, which, in the ordinary form, precipitate from solution at the isoelectric point, whereas the albumins in the ordinary form are not precipitated by acids, but when denatured also have their sedimentation optimum at the isoelectric point.

The isoelectric constants and relative acidity constants at 18° are as follows: Serum globulin, $0{\cdot}36\times10^{-5}$, $2{\cdot}2\times10^{3}$; casein from cow's milk, $1{\cdot}8\times10^{-5}$, $5{\cdot}4\times10^{4}$; gliadin, $6{\cdot}0\times10^{-10}$, $6{\cdot}0\times10^{-5}$; edestin, $1{\cdot}3\times10^{-7}$, 2·8, as compared with albumin $0{\cdot}31\times10^{-3}$, $1{\cdot}6\times10^{3}$. Serum-globulin from different animals gave the same values. G. S.

Composition of Nucleic Acid from Yeast. Katharina Kowalevsky (*Zeitsch. physiol. Chem.*, 1910, 69, 240—264. Compare Levene, Abstr., 1909, i, 54).—Nucleic acid has been prepared from yeast by Altmann's (*Arch. physiol.*, 1899, 526) and by Neumann's method (Abstr., 1899, i, 467; 1900, i, 319), but the product obtained by the latter method is shown to be very impure. The analysis of four specimens prepared according to Altmann gave as a mean N = 12·32% and P = 10·02%. The low nitrogen value indicates that nitrogenous bases had been removed by acid during the preparation. A specimen prepared on a commercial scale gave N = 16·16% and P = 8·65%, and this was used for hydrolysis.

When hydrolysed with nitric acid (10 c.c. of nitric acid, D 1·4, + 10 c.c. of water), the products obtained were guanine, 5·16%; adenine, 7·36%; with sulphuric acid (1 : 2) the products were guanine, adenine, cytosine, and uracil, but no thymine. The uracil is regarded as a secondary product. The nitrogenous portion of the nucleic acid consists of guanine, adenine, and cytosine. The non-nitrogenous portion contains a pentose and not a hexose. The product, C_7H_8O, isolated by Boos (Abstr., 1909, i, 343) in the form of its phenylhydrazone is benzaldehyde, and was present as an impurity in the original phenylbenzylhydrazine used. On the assumption that a molecule of pentose and one of phosphoric acid is present for each molecule of base, the formula $C_{29}H_{42}O_{23}N_{13}P_3$ ($C_5H_5ON_5 + C_5H_5N_5 + C_4H_5ON_3 + 3C_5H_{10}O_5 + 3H_3PO_4 = C_{29}H_{42}O_{23}N_{13}P_3 + 6H_2O$) can be deduced. The amounts of bases and pentose actually isolated are less than those required by such a formula, with the exception of guanine. J. J. S.

Guanylic Acid. Ivar Bang (*Zeitsch. physiol. Chem.*, 1910, 69, 167—168).—Polemical. The author defends his formula for guanylic acid, $C_{44}H_{66}O_{34}N_{20}P_4$, against that proposed by Steudel and Brigl, $C_{10}H_{14}O_8N_5P$. W. D. H.

Protamines. Albrecht Kossel (*Zeitsch. physiol. Chem.*, 1910, 69, 138—142).—*Crenilabrine* is a new protamine separated from the testes of *Crenilabrus pavo*. It yields arginine nitrogen, 42·3%; lysine nitrogen, 11%, and monoamino-nitrogen, 25·1%. Ammonia, tryptophan, and histidine are absent from its cleavage products. It gives Millon's reaction, so tyrosine is probably present. It is therefore not so simple as salmine.

Malenük has prepared sturine from the Caspian sturgeon; the material appears to have suffered in transport, and Malenük has somewhat modified the author's method; he, moreover, found adenine among the cleavage products, which was not the case with sturine made from German sturgeons. W. D. H.

Lipoids. XIV. Leucopoliin. Sigmund Fränkel and Herbert Elias (*Biochem. Zeitsch.*, 1910, 28, 320—329).—From the acetone extract of human brain, a new phosphatide named *leucopoliin*, was separated. It is crystalline, and of constant composition, the formula of its cadmium compound being $C_{374}H_{720}O_{74}N_{10}P_2Cl_4Cd$. It is a deca-amino-diphosphatide, or a penta-amino-monophosphatide. It contains no

methyl group, and yields no base of the choline group. It contains a carbohydrate acid nucleus. It occurs in about equal quantities in white and grey matter, hence its name. W. D. H.

Invertase. Hans von Euler, E. Lindberg, and K. Melander (*Zeitsch. physiol. Chem.*, 1910, 69, 152—166).—A certain quantity of yeast always yields the same amount of invertase whether the dried material is extracted with water, or autolysis is allowed to occur. The preparation of invertase obtained in autolysis contained N 0·36%, C 42·3%, and ash 2·07%. It is the most active preparation so far obtained. If 0·05 gram is dissolved in 5 c.c. of 0·5*N*-sodium dihydrogen phosphate, and 20 c.c. of 20% sucrose solution are added, rotation 0° is reached at room temperature (20°) in fourteen minutes. W. D. H.

Enzymes of Diastase. L. M. Ljalin (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 624—633).—The enzymes in various kinds of malt were obtained by precipitation with ammonium sulphate, and the activity of the various preparations in the breaking down of starch was determined as follows: 10 c.c. of a 10% emulsion of starch were placed in a test-tube, the latter immersed in boiling water for half a minute and shaken. After cooling to 20°, a given quantity (0·1, 0·2 . . . c.c.) of the diastase preparation was added, the tube well shaken, and left for half an hour at 20°; 1/2 c.c. of magenta is now added, and the tube inverted. The starch in the tubes in which the magenta is spread evenly through the solution has been completely broken up. The diastase precipitated with ammonium sulphate is always more active than that precipitated with alcohol, and the diastase from air-dried malt, green malt, and the light-coloured malts employed in the manufacture of light beer are the most active, whilst that from dark malt dried at a high temperature is least active.

The fermenting, coagulating, and proteolytic enzymes as well as the oxydases in the diastase obtained from these and other substances are all of the same order of activity according to the source from which they are prepared. Z. K.

The Deviation of Ferment Action from the Unimolecular Law, with Especial Reference to the Esterases. George Pierce (*J. Amer. Chem. Soc.*, 1910, 32, 1517—1532).—The rate of hydrolysis of ethyl butyrate under the influence of lipase has been measured at 37° for different concentrations of the ester and the enzyme. In some experiments the progress of the reaction was found to be in satisfactory agreement with the equation for a unimolecular change, but this is not generally the case, and the actual course in a particular experiment appears to be determined by the relative concentrations of ester and enzyme. Another factor which is of importance is the acid produced by the hydrolysis, for this apparently diminishes the activity of the enzyme.

In solutions which contain the same amount of ester and acid, the time required for the hydrolysis of a given quantity of ethyl butyrate is inversely proportional to the concentration of the enzyme. For

given enzyme and acid concentrations, the time required for the decomposition of the same amount of ester is independent of the ester concentration, provided that this exceeds a certain limiting value. It thus appears that the activity of the enzyme is independent of the ester concentrations where this is varied between considerable limits.

To account for the observations, it is supposed that the enzyme combines with the ester to form an intermediate compound, the amount of which is proportional to the concentrations of the free enzyme and the ester. This compound then undergoes hydrolysis in accordance with the mass action law.

It is shown that the observed facts are consistent with this hypothesis, and that the action is similar to that which probably takes place in the inversion of sucrose under the influence of invertase.

H. M. D.

Benzophosphide. Percy N. Evans and Jennie Tilt (*Amer. Chem. J.*, 1910, 44, 361—365).—Evans and Vanderkleed (Abstr., 1902, i, 273) have described dichloroacetyl phosphide,

$$CHCl_2 \cdot CO \cdot PH_2,$$

and an account is now given of the preparation and properties of benzoyl phosphide, $C_6H_5 \cdot CO \cdot PH_2$. In view of the analogy of these compounds to the amides, it is suggested that they would preferably be termed "dichloroacetophosphide" and "benzophosphide."

Benzophosphide, prepared by treating benzoyl chloride for six weeks with a current of dry phosphine, generated by the action of phosphorus on alcoholic potassium hydroxide, forms a slightly yellow, or sometimes white, powder. It does not give a definite m. p., but begins to decompose at about 125°. When heated in a current of dry nitrogen, it gradually decomposes above 75° with evolution of phosphine. It is slowly attacked by water or moist air. E. G.

Action of Arsenic Acid on Gallic Acid. Leo F. Iljin (*J. pr. Chem.*, 1910, [ii], 82, 451—462).—Walden, (Abstr., 1899, i, 212) supports Schiff's statement that digallic acid is one of the products of the reaction between gallic and arsenic acids in 95% alcoholic solution. The author has repeated Walden's experiment, but cannot obtain digallic acid, the product free from arsenic being separable by ethyl acetate and petroleum into two fractions, neither of which exhibits the properties of digallic acid; one fraction consists of gallic acid, the other (the smaller) of ethyl gallate.

With regard to the organic arsenic compounds formed in the preceding reaction, the author's results differ from those of Biginelli (Abstr., 1909, i, 801). The arsenical substance obtained by the author in the preceding experiment can be separated, in aqueous ethereal solution, into two fractions by the addition of sodium chloride, one of which does, and the other does not, yield a precipitate with a solution of gelatin. The former is still under investigation; the latter is obtained, after purification, in long needles of the composition $(C_9H_9O_5)_3AsO$. C. S.